

# Carbenes in Matrices—Spectroscopy, Structure, and Reactivity

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## I. Introduction

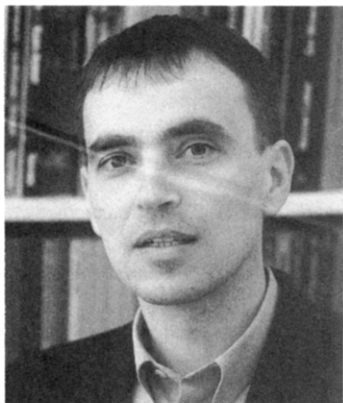
Ever since matrix isolation spectroscopy was used as an analytical tool, carbenes and related species have been a target of this method. Early reports on reactions of methylene in inert gas matrices were published in 1958<sup>1</sup> and 1959,<sup>2</sup> only a few years after the introduction of this technique by Pimentel et al.<sup>3</sup> and Norman and Porter.<sup>4</sup> Since that time matrix spectroscopy has become a well-established technique in the investigation of reactive species<sup>5-7</sup> and numerous papers on the spectroscopy and reactivity of free carbenes appeared. Various aspects of carbenes in matrices have been recently treated in review articles: triplet carbenes,<sup>8</sup> inert gas matrices,<sup>6,9</sup> and reactive matrices.<sup>10</sup> A related field is time-resolved spectroscopy of singlet<sup>11,12</sup> and triplet carbenes<sup>13-16</sup> in solution at ambient temperature. Review articles of general carbene chemistry and spectroscopy<sup>17</sup> and a new volume of *Houben-Weyl*<sup>18</sup> also contain valuable information on carbenes in matrices. Recently a critical compilation of physical data of carbenes and carbene analogues was published by Nefedov et al., which contains information on IR, UV-vis, ESR, and computational data.<sup>19</sup>

The purpose of this review is to collect information on the chemistry and spectroscopy of matrix-isolated carbenes, with emphasis on isolation in inert-gas matrices such as the noble gases or nitrogen. A prerequisite is that the carbenes were characterized by spectroscopic methods, which in the field of matrix isolation are mainly ESR, IR, UV-vis, or fluorescence spectroscopy. Theoretical methods—especially high level *ab initio* methods—are of increasing importance for the interpretation of spectra. Due to the widespread availability of powerful minicomputers and easy to use quantum chemical programs, calculations will become more widespread in the near future. Thus theoretical results on carbenes have been included in this review as long as they were used for comparison with, or interpretation of, experimental data. Although linear carbon molecules ( $C_2$ – $C_6$ ) exhibit carbene-like properties (even  $C_n$  molecules have triplet ground states while odd  $C_n$  molecules are singlets),<sup>20</sup> they are not included in this review.

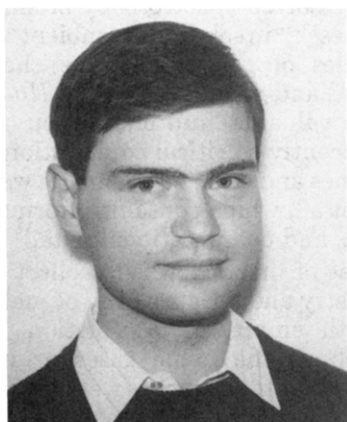
## II. Experimental Methods

### A. Matrix Isolation

Matrix isolation is a powerful method for the study of reactive intermediates. The technique was described in several excellent reviews,<sup>7,21-24</sup> and experimental details will not be given here. Three classes of matrices have been used to isolate and study carbenes: (i) inert



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Götz Bucher was born in Schwäbisch-Gmünd in 1964 and studied chemistry in Heidelberg and Braunschweig, where he presented a thesis on the matrix photochemistry of oxocyclohexadienylidenes. He is currently doing postdoctoral work with Prof. J. C. Scaiano, University of Ottawa, continuing his studies on transient species with the tools of time-resolved laser spectroscopy.

gas matrices, (ii) organic glasses, and (iii) powder matrices. The main differences between these types of matrices are the methods of generating the matrices and the spectroscopic methods which are available for the characterization of trapped species.

(i) Inert gas matrices are produced by codeposition of a noble gas (Ne, Ar, Kr, Xe, where Ar is the most common) or  $N_2$  and a suitable carbene precursor on top of a spectroscopic window placed in a high vacuum system. Carbenes are produced by low temperature (4 K in case of liquid He cooling, around 10 K if closed-cycle He refrigerators are used) photolysis of the matrix-isolated precursors. A requirement for this method is that the precursor can be sublimed without decomposition. By far the most important photolytic precursors are diazo compounds and diazirines. In a few cases carbenes were generated by flash vacuum pyrolysis (FVP) and subsequent trapping of the products with



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excess inert gas at 10–30 K. Typical matrix ratios (inert gas/carbene precursor) are 500–2000, which prevents largely intermolecular reactions of the carbenes. In most experiments the exact matrix ratio is unknown, and the degree of isolation is guessed from the line width in the IR spectra and from the absence of intermolecular reactions of reactive species. If the carbene precursor is very volatile, matrix ratios can be determined directly by mixing with the matrix gas, otherwise microbalances have been used to determine the rates of deposition of less volatile material.<sup>25,26</sup>

Carbenes are thermally stable in Ar matrices as long as the barrier toward rearrangement is higher than several kilocalories per mole and the temperature is kept below the softening point of the matrix. At temperatures higher than 30–50% of the melting point of the matrix diffusion of trapped species is possible and products of intermolecular reactions are formed.<sup>27</sup>

Reactive matrices are produced similarly by doping the inert matrix gas with a reactive component (e.g.  $O_2$ , CO, HCl,  $CH_3OH$ ) or by codeposition of a reactive matrix gas (e.g.  $CO_2$ , ethylene) and carbene precursor on top of a cold window. Reactive matrices allow one to study intermolecular carbene reactions. Reactions of carbenes in  $O_2$ - or CO-doped inert gas matrices lead to the formation of characteristic products such as carbonyl *O*-oxides<sup>28</sup> and ketenes<sup>29</sup> and are used to provide chemical evidence for the presence of a carbene.

(ii) Organic glasses are produced by dissolving the carbene precursor in a suitable solvent and cooling below the freezing point.<sup>27</sup> Organic glasses are generally reactive matrices, although reactions of carbenes might be slow at temperatures below 77 K.<sup>10</sup> Perfluorinated solvents are much less reactive than solvents containing H-atoms, but nevertheless can influence the reactivity of carbenes drastically.<sup>30</sup> Their tendency to crystallize—which prevents optical spectroscopy—limits the usefulness of perfluorinated solvents in low-temperature studies. Because of the low infrared transmission of organic glasses in general, IR studies are restricted to small spectroscopic windows, if possible at all. Organic glasses frequently used to characterize carbenes are listed in Table I.

**Table I. Abbreviations of Solvents Used in Organic Glasses and Powder Matrices**

BZP	benzophenone
DCB	<i>p</i> -dichlorobenzene
DMF	dimethylformamide
DPE	1,1-diphenylethylene crystal
EPA	ether/isopentane/ethanol (5:2:5)
Et <sub>2</sub> O	diethyl ether
EtOH	ethanol
EtI	ethyl iodide
fluorol	fluorolube glass
HCB	hexachlorobutadiene
HFB	hexafluorobenzene
IP	isopentane
neat	precursor as powder matrix
MCH	methylcyclohexane
MTHF	2-methyltetrahydrofuran
PCTFE	poly(chlorotrifluoroethene)
PFDH	perfluorodimethylhexane
TCB	1,2,3-trichlorobenzene

(iii) Powder matrices are generated by irradiation of the neat precursor—or a solution of the precursor in a solvent which does not produce a glass upon freezing—at low temperatures. The carbene is immersed in the microcrystalline solid which forms the matrix. Secondary reactions such as H-abstractions are observed frequently and due to poor optical transparency (IR as well as UV-vis) the only application possible in this type of matrix is ESR spectroscopy. Due to the high density of carbene molecules available by this method, interactions of the triplet molecules to produce quintet pairs can be studied.<sup>31,32</sup>

## B. Spectroscopic Methods

Spectroscopic methods frequently used to characterize carbenes in matrices are (i) IR, (ii) UV-vis, (iii) fluorescence, and (iv) ESR spectroscopy. There are some more special methods, e.g. ENDOR spectroscopy, which will be mentioned in the chapters on individual carbenes.

(i) The absence of intermolecular interactions between trapped species and the absence of rotations (with the exemption of very small molecules such as H<sub>2</sub>O or CH<sub>2</sub>) of isolated molecules leads to narrow line widths and a high gain of intensity of infrared absorptions.<sup>23,24,33–35</sup> This makes IR spectroscopy—especially FTIR spectroscopy with its additional gain in sensitivity—particularly valuable to characterize matrix-isolated carbenes and other reactive species. Isotopic labeling was used extensively to assign infrared absorptions to specific vibrational modes. Most matrix-IR spectra have been obtained in argon or nitrogen matrices, which are of high optical quality in the infrared region.

(ii) Inert gas matrices as well as organic glasses are suitable for recording UV-vis spectra of carbenes. Compared to IR spectroscopy, lower concentrations are required to obtain UV-vis spectra. In several cases “action spectra” have been measured to assure that the same species is observed with different spectroscopic methods. Triplet carbenes, especially with extended  $\pi$ -systems, exhibit weak to medium intensity absorptions in the visible region of the spectrum, which in many cases show vibrational fine structure. Singlet carbenes generally show intense long wavelength absorptions which are very dependent on substituents.

One important aspect of UV-vis spectroscopy is that it provides a link between time-resolved spectroscopy in solution and matrix isolation spectroscopy. UV-vis spectra of the same species obtained by both methods assure that the same chemistry is observed in the solid state and in solution.

(iii) Fluorescence spectra of several carbenes have been obtained in inert gas matrices as well as in organic glasses. Generally the same criteria as for UV-vis spectroscopy are of importance.

(iv) The advantage of ESR spectroscopy is the high selectivity and sensitivity for paramagnetic species such as triplet carbenes, and thus much lower concentrations of carbenes than required for matrix-IR spectroscopy can be easily detected. A large number of carbenes have been characterized by ESR spectroscopy since the pioneering work of Wasserman et al.<sup>36,37</sup> The observation of a stable ESR signal at cryogenic temperatures is generally taken as evidence for the triplet being the ground state of the carbene or at least within a few calories per mole to the ground state. More definite proof comes from the temperature dependence of the ESR signal intensity according to the Curie-Weiss law, but this requires that the carbene be stable to a certain extent at elevated temperatures and no irreversible reactions occur.

The principal information extracted from ESR spectra of triplet molecules in randomly oriented matrices are the zero-field splitting parameters (ZFS parameters)  $D$  and  $E$  (interaction energies in cm<sup>-1</sup>), which measure the magnetic dipole interaction of the unpaired electrons in the absence of an external field.<sup>36,37</sup>

$$D \propto [(r^2 - 3z^2)/r^5] \approx (1/r^3) \quad (1)$$

$$E \propto [(y^2 - x^2)/r^5] \quad (2)$$

$D$  is a measure of the average distance  $r$  of the unpaired electrons and thus allows the determination of the amount of delocalization in carbenes with conjugated  $\pi$ -systems.  $E$  measures the difference of the magnetic dipole interaction along the  $x$  and  $y$  axes (and thus deviation from cylindrical symmetry) and allows one to estimate the bond angle at the carbene center (especially the  $D/E$  ratio is frequently used to estimate the bond angle).<sup>38</sup>  $E$  is related to the  $s$  character of the in-plane singly occupied orbital. For a linear carbene  $E = 0$  is expected (pure  $p$  orbital), while decreasing the bond angle leads to a higher  $s$ -orbital contribution and a larger value for  $E$ .

ESR spectroscopy of triplet carbenes was also used to determine the conformation of geometrical flexible carbenes (see individual carbenes).<sup>39</sup> Thus, from the ZFS parameters important information, such as the geometry at the carbene center and the  $\pi$ -electron spin density, can be drawn.

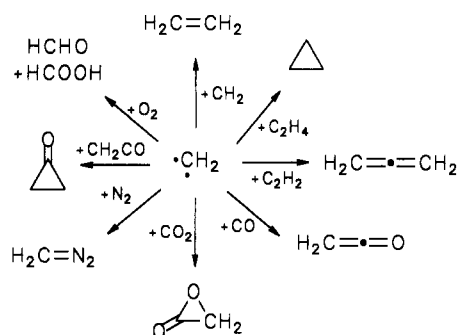
## III. Data of Individual Carbenes

### A. Acyclic Carbenes without Heteroatoms at the Carbene C-Atom

#### 1. Methylene

Methylene—the parent compound of all carbenes—was investigated in several matrix isolation

## Scheme I



studies, the first being reported in 1958 by Milligan and Pimentel<sup>1</sup> and in 1959 by DeMore et al.<sup>2</sup> DeMore et al. photolyzed diazomethane and its deuterated isotopomers  $\text{CHD}_2\text{N}_2$  and  $\text{CD}_2\text{N}_2$ , matrix isolated (0.35 M) in  $\text{N}_2$  at 20 K, and identified ethylene and cyclopropane as the principal products (Scheme I).<sup>2</sup> Although from the IR and UV-vis spectra there was no clear indication of the formation of  $\text{CH}_2$ , some evidence was provided by chemical trapping experiments. Photolysis of  $\text{CH}_2\text{N}_2$  in CO-doped  $\text{N}_2$  matrices produced ketene, which was easily detected by IR spectroscopy. Trapping of carbenes by CO to produce ketenes is now frequently used to identify matrix-isolated carbenes. The rapid thermal reaction of  $\text{CH}_2$  and other carbenes with CO also explains the difficulty in generating carbenes by ketene photolysis in rigid media.

Other intermolecular reactions of  $\text{CH}_2$  studied by DeMore et al. are the reaction with ketene to produce cyclopropanone and the reaction with ethylene to produce cyclopropane (Scheme I).<sup>2</sup> In these experiments the—presumably thermal—formation of the final products and photochemical destruction of  $\text{CH}_2\text{N}_2$  occurs in one step and thus photochemical and thermal reactions are not discriminated.

Milligan and Pimentel<sup>1</sup> first photolyzed (medium-pressure mercury arc lamp) a sample of  $\text{CH}_2\text{N}_2$  (0.125%) in  $\text{N}_2$  at 20 K which produced small amounts of ethylene but no cyclopropane. In the IR spectrum, bands at 1362 and 1114  $\text{cm}^{-1}$  appeared which could not be assigned to known compounds. Afterward the matrix was exposed to a "diffusion operation" by warming it to 30–40 K for a short period of time and cooling it back to 20 K. This procedure caused several of the unassigned bands to decrease in intensity, the bands of ethylene to increase, and new bands, assigned to polyethylene, methane, and propene to grow in. This sequence of experiments—irradiation of the matrix at low temperature and subsequent annealing at higher temperature—clearly demonstrates that irradiation of matrix-isolated  $\text{CH}_2\text{N}_2$  produces reactive species which are trapped in the rigid environment. Warming to 30–40 K permits diffusion of small, matrix-isolated molecules and reactions occur.

Two decades later, Lee and Pimentel reinvestigated the matrix chemistry of methylene.<sup>40,41</sup> The 1362- $\text{cm}^{-1}$  band was assigned to methanimine  $\text{CH}_2\text{NH}$ , which is formed during photolysis of  $\text{CH}_2\text{N}_2$  in inert gas matrices, indicating the high mobility of  $\text{CH}_2$ . Although  $\text{CH}_2\text{NH}$  also exhibits an absorption at 1114.8  $\text{cm}^{-1}$ , evidence was presented that absorptions at 1116 and 819  $\text{cm}^{-1}$  are due to the  $\nu_2$  bending modes of  $\text{CH}_2$  and  $\text{CD}_2$ , respectively, in the triplet ground state.<sup>40</sup> This value

is in good agreement with the 1100–1200- $\text{cm}^{-1}$  value obtained in the gas phase from photoelectron detachment studies of  $\text{CH}_2^-$ <sup>42a</sup> (but see also ref 42b), but considerably higher than the value of  $957 \pm 10 \text{ cm}^{-1}$  obtained by laser magnetic resonance spectroscopy.<sup>42c</sup> Since  $\text{CH}_2$  rotates freely in the matrix, the higher value in the matrix might be assigned to a rotation-vibration line.<sup>42c</sup> Recently Russo et al. calculated  $\nu_1 = 3039$ ,  $\nu_2 = 962$ ,  $\nu_3 = 3281 \text{ cm}^{-1}$  for triplet  $\text{CH}_2$  and  $\nu_1 = 2808$ ,  $\nu_2 = 1307$ ,  $\nu_3 = 2909 \text{ cm}^{-1}$  for singlet  $\text{CH}_2$  using high level *ab initio* methods, in good accord with the available gas-phase data.<sup>321</sup>

A red thermoluminescence with a maximum at 598.7 nm, which occurred on warming a matrix containing  $\text{CH}_2$  above 15 K, was assigned to an emission of electronically excited ethylene (Scheme I).<sup>40</sup> This again demonstrates the high mobility of  $\text{CH}_2$  even in low-temperature inert gas matrices.

The extreme reactivity of matrix-isolated  $\text{CH}_2$  was shown by trapping experiments with molecular  $\text{N}_2$ .<sup>143</sup> Irradiation of  $^{15}\text{N}$ -labeled diazomethane or diazirine in solid  $\text{N}_2$  revealed that  $\text{CH}_2$  is able to react with a neighboring nitrogen molecule in a matrix cage. These experiments also provided information about the matrix sites occupied by the diazomethane molecule. Maier and Reisenauer came to the same conclusion when investigating the photochemistry of diiodomethane in solid nitrogen.<sup>44</sup> Irradiation at 254 nm produced diazomethane (major product), ethylene, acetylene, and the iodomethyl radical via isodiiodomethane and presumably methylene. Thus, diazomethane and diazirine can only produce methylene in rigid matrices if the nitrogen molecule is able to leave the matrix cage.

An early systematic study of the reactions of  $\text{CH}_2$  and simple unsaturated molecules in Ar matrices was conducted by Jacox and Milligan.<sup>45</sup> UV irradiation (cutoff near 220 nm) of  $\text{CH}_2\text{N}_2$  (1%) and acetylene (1%) in Ar at 4 K produced allene, but no cyclopropene or methylacetylene.<sup>45a</sup> When acetylene- $d_2$  and  $\text{CH}_2\text{N}_2$  was used, no scrambling of H and D occurred. A mechanism involving cyclopropylidene as an intermediate was proposed to explain the experimental findings. Irradiation (Pyrex filter) of  $\text{CH}_2\text{N}_2$  and  $\text{CD}_2\text{N}_2$  in solid  $\text{CO}_2$  at 53 K produced CO,  $\text{H}_2\text{CO}$  ( $\text{D}_2\text{CO}$ ), and presumably three further compounds with absorptions between 1894 and 1967  $\text{cm}^{-1}$ .<sup>45</sup> Ethylene was only a minor byproduct, which demonstrates that the degree of isolation of  $\text{CH}_2\text{N}_2$  in  $\text{CO}_2$  is comparable to that in Ar or  $\text{N}_2$ . The absorptions at 1893 and 1900  $\text{cm}^{-1}$  were not shifted on deuteration but exhibited red-shifts of 35  $\text{cm}^{-1}$  when  $^{13}\text{CO}_2$  was used in the experiments. Short wavelength UV irradiation caused the intensity of these bands to decrease and CO and  $\text{CH}_2\text{O}$  to build up. On the basis of this evidence the formation of  $\alpha$ -lactone as an intermediate in the carboxylation of  $\text{CH}_2$  was proposed (Scheme I).

The oxygenation of  $\text{CH}_2$  was investigated by Lee and Pimentel.<sup>41</sup> Matrix samples with  $\text{CH}_2\text{N}_2/\text{Ar}/\text{O}_2$  were irradiated at 8 K and subsequently annealed at higher temperatures. The main products identified by IR spectroscopy were formaldehyde  $\text{HCHO}$ , formic acid  $\text{HCOOH}$ , and CO. On warming to 35 K and recooling, absorptions assigned to  $\text{HCHO}$  and  $\text{HCOOH}$  slightly increased in intensity. During warming the matrix a chemiluminescence was observed which was attributed

Table II. ESR Data of Methylene and Alkylcarbenes (Chart I)

carbene	matrix <sup>a</sup>	T, K	D/hc, cm <sup>-1</sup>	E/hc, cm <sup>-1</sup>	E/D	comments	ref
CH <sub>2</sub>	Xe	4.2	0.69	0.003	0.004		47
CH <sub>2</sub>	Xe	4	0.6636	<0.002	<0.003	two sites with different mobility	46
			0.6881	0.00346	0.005		
CHD	Xe	4	0.7443	0.00640	0.0086		49
CD <sub>2</sub>	Xe	4	0.7563	0.00443	0.0059		49
	Xe	4.2	0.759	0.0044	0.0058		50
<sup>13</sup> CD <sub>2</sub>	Xe	4	0.961	0.0103	0.0107	D-C-D angle 137° (hfs)	51
	Xe	4.2	0.760	0.0043	0.0057	D-C-D angle 137.7°	50
4	MTHF	20	0.689	0.039	0.057	C-C-C angle 143° (E/D ratio)	60
5	neat	14	0.6823	0.038	0.056	C-C-C angle 152° (hfs)	61
6a	PFDH	4	0.712	0.021	0.029	C-C-H angle 160°	63
6b	PFDH	4	0.723	0.027	0.037	C-C-H angle 160°	63
6c	PFDH	4	0.72	0.024	0.033	C-C-H angle 160°	63
7	PFDH	4	0.7444	0.0437	0.059	C-C-H angle 140°	63
8	MTHF	5	0.6860	0.0302	0.044		66a
9	MTHF	5	0.6820	0.0293	0.043		66a

<sup>a</sup> See Table I.

to one or several excited states of HCOOH.<sup>41</sup>

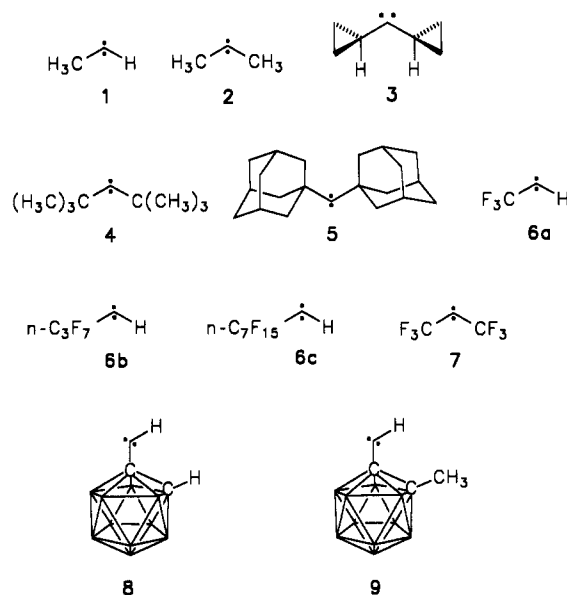
The first ESR studies on methylene appeared in 1970 and demonstrated experimentally that the ground state of CH<sub>2</sub> is a triplet state,<sup>46,47</sup> in accordance with gas-phase investigations<sup>42</sup> and *ab initio* theory.<sup>48</sup> (The most accurate value for the singlet-triplet splitting of CH<sub>2</sub> obtained from far-infrared laser magnetic resonance spectroscopy is  $9.05 \pm 0.06$  kcal/mol.<sup>42d</sup>) Methylene and several of its isotopomers (CHD,<sup>49</sup> CD<sub>2</sub>,<sup>49</sup> <sup>13</sup>CH<sub>2</sub>,<sup>50,51</sup> and <sup>13</sup>CD<sub>2</sub>,<sup>50,51</sup>) were generated by irradiation of isotopically labeled diazomethane or diazine in Xe at 4 K or 77 K (Table II). Both precursors produced the same ESR spectra independent of the temperature, which gives strong evidence for the formation of CH<sub>2</sub>. In addition, labeling the carbon nucleus with <sup>13</sup>C results in a splitting of the ESR lines to doublets, as expected if only one C-atom is present in the triplet species.<sup>50,51</sup> Three H/D isotopomers (CH<sub>2</sub>, CHD, and CD<sub>2</sub>) were detected, which proves that two chemically equivalent hydrogen atoms are present. Thus, there is no doubt that CH<sub>2</sub> is indeed the triplet species that was observed in the ESR experiments.

ESR spectra have been particularly valuable in determining the H-C-H bond angle of CH<sub>2</sub>. The interpretation of the ESR spectra is complicated by the fact that CH<sub>2</sub> occupies two different sites with different mobility in Xe, which produce two different spectra. Analysis of the zero-field parameters *E* reveals a bond angle of 136° as the most probable value.<sup>46</sup> Independently, a very similar value was deduced from the hyperfine splitting in <sup>13</sup>CD<sub>2</sub>.<sup>50,51</sup>

## 2. Alkylcarbenes

Due to the low barrier of 1,2-H shifts, most carbenes with  $\alpha$ -H atoms are unstable even under the conditions of matrix isolation. *Ab initio* calculations (MP2/6-31G\*) predict an activation energy of only 0.9 kcal/mol for the 1,2-H shift in methylcarbene (1) but of 6.0 kcal/mol in dimethylcarbene (2)<sup>52</sup> (Chart I). The rates of hydrogen shifts might be enhanced by quantum mechanical tunneling (QMT), and therefore the experimental barriers are estimated to be even lower. In an attempt to matrix-isolate methylcarbene (1), Seburg and McMahon investigated the photochemistry of diazoethane and methyldiazirine in a variety of inert gas matrices.<sup>53</sup> ESR as well as IR and UV-vis spec-

Chart I



troscopic studies failed to provide experimental evidence of 1. However, in CO-doped matrices methyl ketene was formed, indicating that CO trapping by singlet 1 can compete with hydrogen migration, while ISC to the triplet ground state does not. Modarelli and Platz were able to show in a laser flash photolysis (LFP) experiment, using the pyridine ylide probe method, that deuteration increased the yield of trapable methylcarbene (1).<sup>54</sup> The lifetime of singlet methylcarbene-d<sub>4</sub> in pentane at room temperature was estimated to 500 ps and the barrier to its isomerization to less than 2.3 kcal/mol. The same authors presented evidence that dimethylcarbene (2) is also a true intermediate with a finite lifetime in solution at room temperature by trapping the carbene with pyridine in an LFP experiment.<sup>55</sup> Thus there is a change that 2 can be trapped in low temperature matrices.

The first singlet dialkylcarbene that has been directly characterized in a matrix is dicyclopropylcarbene (3).<sup>56</sup> Irradiation ( $\lambda = 334$  nm) of dicyclopropyldiazirine in N<sub>2</sub> at 6 K produced dicyclopropyldiazomethane and carbene 3 with the strongest IR absorption at 802 cm<sup>-1</sup> and a broad UV-vis maximum at 490 nm. The observed IR spectrum was in good agreement with the MP2/6-31G(d) calculated spectrum. Subsequent irradiation

with  $\lambda = 475$  nm produced ethylene, cyclopropylacetylene, and 1-cyclopropylcyclobutene. In a CO-doped matrix dicyclopentyl ketene was produced.

Other carbenes bearing  $\alpha$ -H atoms which have been trapped in matrices are triplet phenylmethylcarbene (phenylethylidene) (56),<sup>57</sup> phenylcarbenes 58–62 and 64 (Chart IV), and the singlet carbenes cyclopropylchlorocarbene (201),<sup>58</sup> benzylchlorocarbene (202),<sup>59</sup> (Chart XIV), and methoxymethylcarbene (211) (Chart XV).

Several alkylcarbenes without  $\alpha$ -H atoms were generated and spectroscopically characterized in matrices. Di-*tert*-butylcarbene (4) is sufficiently stable to be observed in MTHF glass at 20 K by ESR spectroscopy (Table II).<sup>60</sup> At temperatures above 70 K the carbene disappeared irreversibly. From the  $E/D$  ratio a bond angle at the carbene center of  $143^\circ$  was estimated,<sup>60</sup> which might be a lower limit.<sup>61</sup> Irradiation of neat di-*tert*-butyldiazomethane at 14 K and subsequent warming to room temperature gave mainly products typical of a singlet carbene.<sup>60</sup>

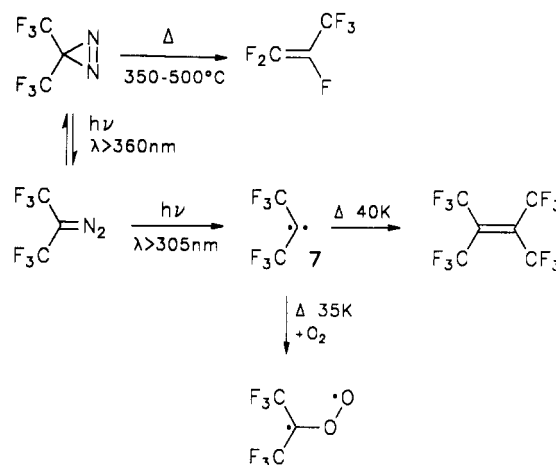
Unlike 4, diadamantylcarbene (5) shows substantial triplet reactivity.<sup>61,62</sup> Irradiation of diadamantyldiazomethane labeled with  $^{13}\text{C}$  at the central position produced carbene [ $^{13}\text{C}$ ]-5 (Table II). The Curie law was obeyed, and from the hyperfine splitting a bond angle of  $152^\circ$  was estimated. The wide angle enforced by steric interactions stabilizes the triplet state of 5 compared to the singlet.<sup>61</sup>

In contrast to the simple alkylcarbenes, fluorinated alkylcarbenes are thermally more stable and have been characterized in several low-temperature studies. Wasserman et al.<sup>63</sup> demonstrated that (trifluoromethyl)carbene (6a), (heptafluoropropyl)carbene (6b), (pentadecafluoroheptyl)carbene (6c), and bis(trifluoromethyl)carbene (7)—produced by irradiation of the corresponding diazo compounds in perfluorodimethylhexane at 4 K—have triplet ground states (Table II). From the ESR data, bond angles at the carbene centers were estimated to  $160^\circ$  (6a–c) and  $140^\circ$  (7), which reveals that an additional  $\text{CF}_3$  group reduces the angle at the carbene center. In the same study during warmup of solutions containing both 7 and  $\text{O}_2$  a strong chemiluminescence was noted, which was identical to the phosphorescence of hexafluoroacetone.<sup>63</sup>

Irradiation of bis(trifluoromethyl)diazirine<sup>64</sup> or bis(trifluoromethyl)diazomethane<sup>65</sup> in Ar at 12 K produced 7, and its IR spectrum was recorded (Scheme II). FVP (0.001 Torr, 350–500  $^\circ\text{C}$ ) of the diazirine gave only hexafluoropropene and no carbene, indicating a rapid 1,2-shift of fluorine atoms at high temperatures.<sup>64</sup> Warming of matrix-isolated 7 to 40–45 K caused the IR bands assigned to the carbene to disappear and bands of the carbene dimer to grow in. In the presence of CO (Ar/CO = 5/1) bis(trifluoromethyl) ketene was formed.<sup>64</sup>

The reaction of 7 with  $^3\text{O}_2$  in  $\text{O}_2$ -doped Ar matrices has also been reported.<sup>65</sup> Annealing a 1%  $\text{O}_2$ -doped Ar matrix containing 7 for several minutes at 35–40 K leads to the complete disappearance of the carbene and formation of hexafluoroacetone *O*-oxide (Scheme II). The O–O stretching mode of the carbonyl oxide is found at 997  $\text{cm}^{-1}$  and red-shifted by 35  $\text{cm}^{-1}$  in the  $^{18}\text{O}_2$ -labeled compound. The carbonyl oxide is very photolabile, and irradiation with  $\lambda > 590$  nm produced hexafluoroacetone as the principal product. The rapid formation of a

**Scheme II**



carbonyl oxide in a thermal reaction at low temperature provides further evidence for the carbene being produced on irradiation of the diazo precursor and suggests a triplet ground state for 7,<sup>65</sup> in accordance with ESR studies.<sup>63</sup> In contrast to the clean thermal oxygenation of the carbene, the in-cage photooxidation of the diazo precursor leads to a variety of products such as  $\text{CO}_2$  and  $\text{COF}_2$ , which shows that C–F bonds are cleaved under these conditions.

During annealing the matrix a chemiluminescence was observed,<sup>65</sup> in accordance with the earlier observation of Wasserman et al.<sup>63</sup> in organic glasses. The chemiluminescence starts at very low temperature (warming the matrix from 10 to 15 K) and was identified as phosphorescence of hexafluoroacetone. From these experiments it was concluded that the chemiluminescent step is the combination of carbene 7 and triplet oxygen atoms leading to triplet hexafluoroacetone.<sup>65</sup>

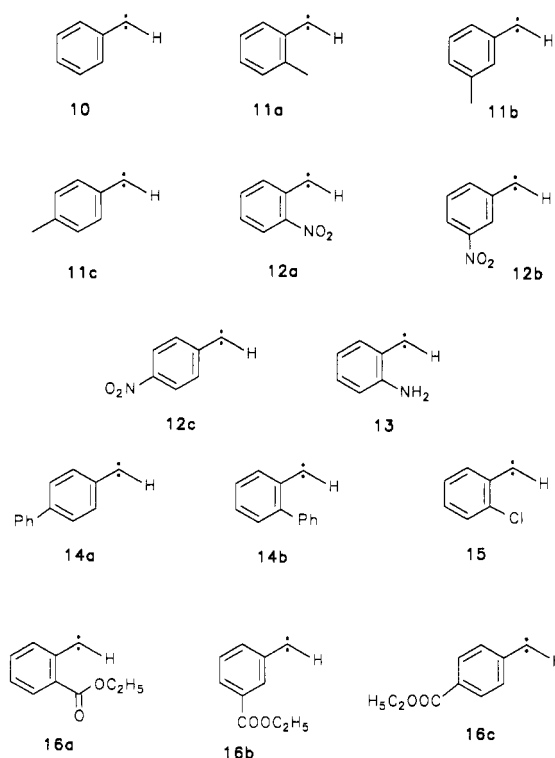
Hutton and Roth reported ESR data of the two *o*-carboranylcarbenes 8 and 9 in MTHF at 5 K (Table II).<sup>66a</sup> The observation of a triplet ESR spectrum was taken as evidence for the triplet being the ground state or lying within a few calories of the ground state. A  $\pi$ -spin density of 0.9 at the carbene center—corresponding to a largely localized  $\pi$ -system—was estimated from the large value of the ZFS parameter  $D$ . In contrast to the linear boron-substituted 3-*o*-carboranylcarbenes 215 and 216, a substantial  $E$  value was observed for 8 and 9 (Table II), indicating a bent carbene structure. From *ab initio* calculations on several model carboranylcarbenes McKee concluded that (i) the singlet–triplet splitting is small in these carbenes, (ii) insertion into the C–H bond of adjacent  $\text{CH}_3$  groups is accompanied with a substantial activation barrier, and (iii) the fused cyclopropenyl ring/cage system is more stable than the carbene.<sup>66b</sup> The stability of 8 and 9 might be associated with the extra stability of a closo 12-vertex cage compared to the expanded 13-vertex cage.

### 3. Phenylcarbene

Phenylcarbene (10, Chart II) is a triplet ground state carbene, which has been characterized in the course of a number of spectroscopic studies employing matrix isolation in noble gases, organic glasses, single crystals, or polycrystalline samples. The most common precursor for 10 is phenyldiazomethane, but the sodium



Chart II



salt of benzaldehyde tosylhydrazone<sup>67a</sup> and diazido-phenylmethane<sup>67b</sup> were also successfully used for its generation.

The ESR spectrum of 10 was reported early in the 1960s by Trozzolo, Wasserman, Murray, and Yager.<sup>68,69</sup> Zero-field splitting parameters  $D = 0.518 \text{ cm}^{-1}$  and  $E = 0.024 \text{ cm}^{-1}$  are indicative of spin delocalization within the phenyl ring (albeit less than in diphenylcarbene) and show that 10 cannot be a linear molecule. Confirmation of this conclusion was obtained from an investigation of  $^{13}\text{C}$ -hyperfine splitting, using 1- $^{13}\text{C}$  labeled phenyldiazomethane.<sup>69</sup> More recently, the fluorescence spectrum of 10 in 3-methylpentane matrix at 77 K was measured by Haider et al.<sup>70</sup> in a laser-induced fluorescence (LIF) study. This technique had to be applied as phenylcarbene is stable in organic matrices only on a time scale of minutes. Emission maxima were found at 445 and 476 nm. Prior to this observation, the formation of 10 from 2,3-diphenyl-oxirane had been postulated by Becker et al.<sup>71</sup> The emission spectrum ( $\lambda_{\text{max}} = 389$  and 414 nm) reported by these authors, however, fits neither the LIF spectrum of Haider, nor is it consistent with the absorption

spectrum measured by Chapman (see below); thus there is severe doubt whether Becker's assignment of 10 is correct. A way to circumvent the difficulties imposed by the high reactivity of phenylcarbene is to utilize noble gas or nitrogen matrices; it was done first in 1982 by Chapman et al.,<sup>72</sup> who were able to record the infrared and UV-vis absorption spectra of 10. The latter spectrum exhibits a long-wavelength band system with a rich fine structure and a prominent maximum at 430 nm, while the IR spectrum of 10 offers much less characteristic features. Phenylcarbene is unstable toward visible light irradiation ( $\lambda > 416 \text{ nm}$ ); it rearranges to yield cyclohepta-1,2,4,6-tetraene. The reaction is apparently not straightforward, and it will be discussed in some detail later. Subsequent studies on 10 in Ar matrix dealt with its reaction with triplet oxygen.<sup>73,74</sup>

All three isomeric tolyldiazomethanes yield benzocyclobutene and styrene on thermolysis. This intriguing result prompted a number of investigations,<sup>75</sup> utilizing  $^{13}\text{C}$ -isotopic labeling, or matrix isolation spectroscopy. In the course of such a matrix study, Chapman et al.<sup>76</sup> were able to observe the three tolylcarbenes by UV-vis, IR, and ESR spectroscopy. The least stable member of the family proved to be *o*-tolylcarbene (11a), which undergoes a very facile thermal hydrogen shift to yield *o*-xylene,<sup>57</sup> but *m*- and *p*-tolylcarbene (11b and 11c) also rearrange upon irradiation (see section IV.A). The spectroscopic properties of the three tolylcarbenes are very similar, all of them exhibiting a richly structured absorption extending in the visible region from about 395 to 450 nm. The IR spectra do not show any particularly characteristic absorptions, and from the ESR spectra zero-field splitting parameters around  $D = 0.51 \text{ cm}^{-1}$  and  $E = 0.024\text{--}0.025 \text{ cm}^{-1}$  can be derived (Table III). Further phenylcarbene derivatives that have been characterized include (3- and 4-nitrophenyl)carbene (12b<sup>77</sup> and 12c<sup>77</sup>), as well as 4- and 2-biphenylcarbene (14a<sup>77</sup> and 14b<sup>78</sup>), and (2-chlorophenyl)carbene (15), which was characterized in Ar matrix by IR and UV spectroscopy.<sup>79</sup> 12b,c and 14a,b were observed by means of ESR spectroscopy; as expected, relative to 10 the  $D$  value decreases in 12c and 14a due to extended  $\pi$ -delocalization, but surprisingly it is higher in 12b!

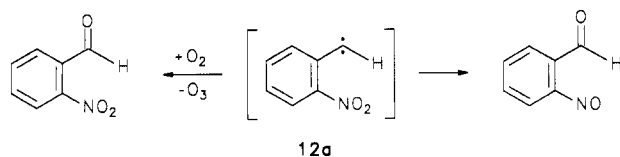
Ortho-substituted carbenes such as 11a are in many cases subject to atom transfer from the ortho substituent to the carbene center and thus labile even under the conditions of matrix isolation. (2-Nitrophenyl)carbene (12a) and (2-aminophenyl)carbene (13) are two examples of this class of carbenes.<sup>80</sup> Irradiation ( $\lambda > 350$

Table III. Spectroscopic Properties of Phenylcarbene Derivatives (Chart II)

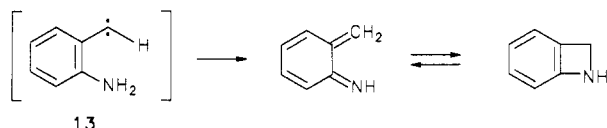
carbene	matrix <sup>a</sup>	<i>T</i> , K	<i>D</i> /hc, cm <sup>-1</sup>	<i>E</i> /hc, cm <sup>-1</sup>	<i>E</i> / <i>D</i>	absorption $\lambda$ , nm	emission $\lambda$ , nm	ref(s)
10	DCB	77	0.5150	0.0251	0.04873			69
	fluorol	77	0.518	0.024	0.046			68
	Ar	10				430	455, 476	72, 70
11a	Ar	10–15	0.503	0.0253	0.05030	413–450		76
11b	Ar	10–15	0.517	0.0246	0.04758	394–448		76
11c	Ar	10–15	0.516	0.0240	0.04651	395–444		76
12b	<i>b</i>		0.5230	0.0243	0.04646			77
12c	<i>b</i>		0.4859	0.0224	0.04610			77
14a	<i>b</i>		0.4788	0.0277	0.05785			77
14b	Et <sub>2</sub> O	77	0.510	0.020	0.03922			78
15	Ar	10				456, 308		79

<sup>a</sup> See Table I. <sup>b</sup> Not specified.

nm) of (2-nitrophenyl)diazomethane matrix-isolated in argon at 10 K provided 2-nitrosobenzaldehyde by intramolecular oxygen migration.<sup>80a</sup> Carbene 12a could be trapped as 2-nitrosobenzaldehyde in 20% oxygen-doped argon matrices, but direct spectroscopic characterization of the carbene was not possible.



Similarly, photolysis ( $\lambda = 544$  nm, argon, 11 K) of (2-aminophenyl)diazomethane produced 6-methylene-2,4-cyclohexadien-1-imine, which on shorter wavelength photolysis was converted to benzazetine.<sup>80b</sup>



The chemistry of the three isomeric (carbomethoxyphenyl)carbenes 16 was subject of a communication by Tomioka et al.<sup>81a</sup> The ortho isomer 16a could not be isolated, but reacted intramolecularly with the carbonyl function to yield an ylide. 16b and 16c could be obtained, but spectroscopic data were not given. Finally, the radical cation derived from phenylcarbene was observed and published by Miyazaki et al.<sup>81b</sup> [ $\gamma$ -Irradiation of phenyldiazomethane in *n*-butyl chloride at 77 K yields its radical cation ( $\lambda_{\max} = 515$  nm), which is destroyed upon irradiation, forming  $10^{+}$  ( $\lambda_{\max} = 475$  nm)].

#### 4. Diphenylcarbene

The chemistry of diphenylcarbene 17 has been extensively investigated in Ar matrix as well as in Shpol'skii matrices. Additionally, a number of studies were published utilizing benzophenone (BZP) or 1,1-diphenylethylene (DPE) single crystals as ordered matrices. The literature includes numerous product studies, UV-vis (Table IV), ESR (Table V), ENDOR, and IR spectroscopic studies; an overwhelming amount of information has been gathered, and much of this work has already been reviewed.<sup>19,77,82-84</sup> The wealth of knowledge may be due to the fact that with diphenyldiazomethane a precursor is available which is prepared and handled in a relatively simple way and which yields the carbene under very mild photolytic conditions. 17 has also been generated photolytically from triphenyl-<sup>71,85</sup> and tetraphenyloxirane,<sup>71,86,87</sup> from 2,2,4,4-tetraphenyloxetan-3-one,<sup>86,87</sup> from the sodium salt of benzophenone tosylhydrazide,<sup>67a,88</sup> and from diazido-<sup>67b</sup> and dichlorodiphenylmethane [in the presence of tetrakis(dimethylamino)ethylene].<sup>89</sup> For most of the carbene studies it is also a benefit that 17 (Chart III), unlike phenylcarbene, does offer the advantage of photostability under short wavelength photolytic conditions.

Among arylcarbenes, diphenylcarbene was the first to be characterized spectroscopically. Attempts to obtain spectral information started in the late 1950s, and research activities have not come to an end today.

*a. ESR Spectroscopy.* The first ESR spectroscopic data for 17 were presented in 1962 by Murray, Trozzolo, Wasserman, Cramer, and Yager,<sup>68,90,91</sup> and, practically at the same time, by Brandon, Closs, and Hutchison (Table V).<sup>92</sup> In these studies Wasserman et al. utilized fluorolube glass as matrix, whereas Closs et al. measured the ESR spectrum of 17 in a benzophenone single crystal at 77 K. This work confirmed Skell's prediction<sup>93</sup> that 17 should be a triplet ground state molecule. Closs et al. found ZFS parameters of  $D = 0.4050$  cm<sup>-1</sup> and  $E = 0.0186$  cm<sup>-1</sup>, which showed for the first time that considerable spin delocalization occurs within the molecule and that there is a significant deviation from the predicted linear  $D_{2d}$  symmetry.<sup>93</sup> Another important finding from Wasserman's studies<sup>68</sup> was the observation of a bright blue chemiluminescence upon warming of 17 in O<sub>2</sub>-doped glasses which was attributed to benzophenone phosphorescence (this was later confirmed by us<sup>74</sup>). Using 1-<sup>13</sup>C-enriched samples, both Closs<sup>92</sup> and Wasserman<sup>69</sup> could also measure the <sup>13</sup>C-hyperfine splitting; but proton hyperfine splitting was not observed. The ESR spectrum of 17 as a function of the matrix material was examined by Trozzolo, Wasserman, and Yager.<sup>94</sup> Brandon et al. studied the ESR spectrum of 17 in a benzophenone single crystal in greater detail.<sup>95</sup> More recently, a study of 17 in BZP was published by Sixl et al.,<sup>96</sup> who found a change in the ESR spectrum upon warming the crystal up to 60 K, which is caused by release of the N<sub>2</sub> molecules. 17 is assumed to reside substitutionally into benzophenone crystals, so that the individual 17 molecules are well aligned (one has to pay attention, however, to the fact that benzophenone undergoes a phase transition on cooling from 77 to 2 K<sup>97</sup>). Consequently, the fine structure tensors shows a large anisotropy with respect to the orientation of the external magnetic field. One can make further use of this alignment in electron-nuclear double resonance (ENDOR) experiments; in the case of 17, this was done first by Hutchison and Kohler.<sup>98</sup> ENDOR studies on 17 were also published by Doetschman and Hutchison (in 1,1-diphenylethylene at 77 K),<sup>99</sup> as well as by Anderson and Kohler (in benzophenone at 2 K).<sup>100</sup> The results can be summarized as follows: 17 is a bent molecule with C<sub>2</sub> symmetry (in DPE;<sup>99</sup> in BZP at 2 K only C<sub>1</sub> symmetry is observed;<sup>100</sup> in this case the two benzene rings have slightly different angles to the C8-C1-C2 plane). The C8-C1-C2 bond angle is 140.0°,<sup>100</sup> (ref 78,<sup>99</sup> 148°) and the phenyl substituents are rotated out of the C8-C1-C2 plane by 36°<sup>99</sup> (ref 79<sup>100</sup> gives 29.9° and 26.2°). The spin density at C1 was calculated to be 0.620; positive spin density is also found at the ortho and para positions.<sup>100</sup> This is already a quite detailed picture of the reactive species diphenylcarbene!

Another approach to obtain aligned samples of 17 is to irradiate the diazo precursor (*a priori* without orientation, in an organic glass) with plane polarized light. According to Dunkin et al.,<sup>101</sup> this leads to a well-observable polarization of the ESR spectrum, and it also allows the determination of the orientation of the transition moment leading to photofragmentation of the diazo compound within the molecular framework: the diazo compound must have absorbed the light along the CNN axis.



Table IV. UV-Vis Spectroscopic Data of Diphenylcarbenes (Chart III)

carbene	matrix <sup>a</sup>	T, K	$\lambda$ , nm			$t_{1/2}$ , ns	ref
			absorption <sup>b</sup>	excitation <sup>c</sup>	emission <sup>d</sup>		
17	MTHF	77	300,465		480		112
	BZP	4.2	448,465				116
	BZP	4.2	471.18 <sup>e</sup>				116
	MCH	77			483 <sup>e</sup>	121	122
	BZP	10				320–360	120
	BZP	25				140	119
	MCH	77				108	117
	EtOH	77				87	117
	EtOH/EtI	77				72	117
	BZP	4.2	463.5				116
$d_{10-17}$	BZP	4.2	469.55 <sup>e</sup>				116
18	MTHF	77	301,472		487		112
	MTHF	77	311,472		487		121
	MCH	77			486 <sup>e</sup>		122
19	MTHF	77		335–345	495		112
	MTHF	77	322,480		495		121
	MCH	77 <sup>f</sup>	324,458	320,420,478	489	77.1	118
	EtOH	77 <sup>f</sup>	320,380,460	328,410,480	495	79.4	118
	EtOH/EtI	77 <sup>f</sup>	323,422,475	323,422,475	492	74.5	118
20	MTHF	77		335–345	507		112
	MCH	77 <sup>f</sup>	330,485	330,485	504	66.8	118
	EtOH	77 <sup>f</sup>	330	328		72.1	118
	DMF	77 <sup>f</sup>				59	118
21	MTHF	77	311,475		487	110	112
	MTHF	77	317,475		487		121
	BZP	4.2	482.57 <sup>e</sup>				116
	MCH	77			492 <sup>e</sup>		122
22	MCH	77			500 <sup>e</sup>		122
23	MTHF	77	316,475		488		112
	MTHF	77	319.5,477		488	91	121
	BZP	4.2	483.91 <sup>e</sup>				116
	MCH	77			491 <sup>e</sup>	32	122
24	MCH	77 <sup>f</sup>	270,328,480	270,326	498	11.4	118
	EtOH	77 <sup>f</sup>	270,325,480	268,324	499	11.4	118
	EtOH/EtI	77 <sup>f</sup>	483	284,327,483	497	11.7	118
25	MTHF	77	265,370,555				112
26	MCH	77 <sup>f</sup>	325,390				118
	EtOH	77 <sup>f</sup>	295,365,565				118
27	MTHF	77		355	555		112
	MCH	77			557 <sup>e</sup>		122
28	MTHF	77	332,496		510		121
	MCH	77 <sup>f</sup>	320,460	325,460,475	510	84.0	118
	EtOH	77 <sup>f</sup>	330,460,495	330,460,495	510	74.6	118
	EtOH/EtI	77 <sup>f</sup>	330,460,495	330,458,495	511	66.4	118
	MCH	77			510 <sup>e</sup>	88	122
29	MCH	77 <sup>f</sup>	332,470,510	332,425,510	526	69.5	118
	EtOH	77 <sup>f</sup>	334,475,510	333,475,512	530	65.9	118
	EtOH/EtI	77 <sup>f</sup>	336,473,512	336,475,510	530	59.5	118
39	MCH	77			492 <sup>e</sup>	109	122
40	MCH	77			482 <sup>e</sup>	830	122
41	MCH	77			486 <sup>e</sup>	1600	122
42	MCH	77			516 <sup>e</sup>		122

<sup>a</sup> See Table I. <sup>b</sup> Absorption maxima. <sup>c</sup> Absorption maxima derived from excitation spectra. <sup>d</sup> Emission maxima. <sup>e</sup> 0–0 transition. <sup>f</sup> Variable-temperature study 4–95 K, data in table obtained at 77 K.

Several studies dealt with the influence of para substituents on the ESR spectrum of diphenylcarbene (Table V). All of the DPC derivatives investigated so far proved to be triplet ground state molecules, as was shown by means of a Curie plot in many cases. Humphreys and Arnold examined a series of 4-substituted and 4,4'-disubstituted DPC derivatives, laying particular stress on the investigation of 4-donor-4'-acceptor substituted systems.<sup>88,102,103</sup> As a general trend, para substitution of the DPC molecule results in a decrease of the  $D$  parameter, which is proportional to  $1/r^3$ ,  $r$  being the average separation of the unpaired electrons. This effect, which is obviously due to extended  $\pi$ -delocalization of spin density, is never very large; the most prominent deviation from the  $D$  value

of 17 is observed in donor-acceptor-substituted molecules like 34.<sup>88</sup> Humphreys and Arnold explained this observation in terms of merostabilization, i.e. participation of charge-separated mesomeric structures with favorable energy (cf. Katritzky et al.<sup>104</sup>). It is evident that electronic factors exert significant influence on carbene structure, but steric hindrance imposed by bulky ortho substituents may equally alter its properties, the best examined example being dimesitylcarbene (41). Its ESR spectrum, which was reported by Nazran, Griller, and co-workers,<sup>105–107</sup> shows zero-field splitting parameters of  $D = 0.3460 \text{ cm}^{-1}$  and  $E = 0.0082 \text{ cm}^{-1}$ , which are significantly lower than in other diphenylcarbene derivatives. Probably in 41 the aryl groups are close to perpendicular, as dimesityldiazo-

Table V. ESR Data of Diphenylcarbenes (Chart III)

carbene	matrix <sup>a</sup>	T, K	D/hc, cm <sup>-1</sup>	E/hc, cm <sup>-1</sup>	E/D	ref
17	BZP	77	0.4055	0.0194	0.0478	69
	BZP	77	0.4050	0.0186	0.0459	92
	BZP	77	0.40505	0.01918	0.0474	95
	DPE	4	0.39644	0.01516	0.0382	98
	BZP	80 <sup>b</sup>	0.406	0.019	0.0468	96
	BZP	2	0.407783	0.020625	0.0506	97
	fluorol	77	0.401	0.0186	0.0464	68
	MCH	77	0.4053	0.0190	0.0469	85
	MCH/IP	5	0.4088	0.0170	0.0416	102
	c	c	0.4071	0.0188	0.0462	77
18	MCH/IP	5	0.4043	0.0191	0.0472	102
19	MTHF	10	0.406	0.0193	0.0475	108
	neat	10	0.408	0.0180	0.0441	108
20	MCH/IP	5	0.4022	0.0189	0.0470	102
	MTHF	10	0.407	0.0198	0.0486	108
	neat	10	0.408	0.0197	0.0483	108
21	c	c	0.4029	0.0194	0.0482	77
22	MTHF	10	0.399	0.0194	0.0486	108
	neat	10	0.398	0.0194	0.0487	108
23	c	c	0.3921	0.0191	0.0487	77
25	neat	77 <sup>d</sup>	0.3778	0.0173	0.0458	88
26	THF	77 <sup>d</sup>	0.3773	0.0177	0.0469	88
28	MCH/IP	5	0.3906	0.0180	0.0461	102
	MCH/IP	77 <sup>d</sup>	0.3906	0.0193	0.0494	88
29	MCH/IP	77 <sup>d</sup>	0.3879	0.0178	0.0459	88
30	MCH/IP	77 <sup>d</sup>	0.3774	0.0172	0.0456	88
31	neat	77 <sup>d</sup>	0.3518	0.0163	0.0463	88
32	THF	77 <sup>d</sup>	0.3696	0.0171	0.0463	88
33	THF	77 <sup>d</sup>	0.3611	0.0172	0.0476	88
34	THF	4 <sup>e</sup>	0.3551	0.0164	0.0462	88
35	THF	77 <sup>d</sup>	0.3994	0.0178	0.0446	88
36	THF	77 <sup>d</sup>	0.3876	0.0168	0.0433	88
37	MTHF	77 <sup>d</sup>	0.3748	0.0180	0.0480	88
38	neat	10	(triplet)			109
41	IP/Et <sub>2</sub> O	5.8	0.3460	0.0082	0.0237	105
41 <sup>f</sup>	IP/Et <sub>2</sub> O	5.8	0.3558	0.0125	0.0351	105

<sup>a</sup> See Table I. <sup>b</sup> Irreversible change at 106 K. <sup>c</sup> Not specified.

<sup>d</sup> Variable-temperature study 4–30 K, ZFS parameters at 77 K.

<sup>e</sup> Signal not strong enough at higher temperature. <sup>f</sup> Before annealing (measured at 6 K).

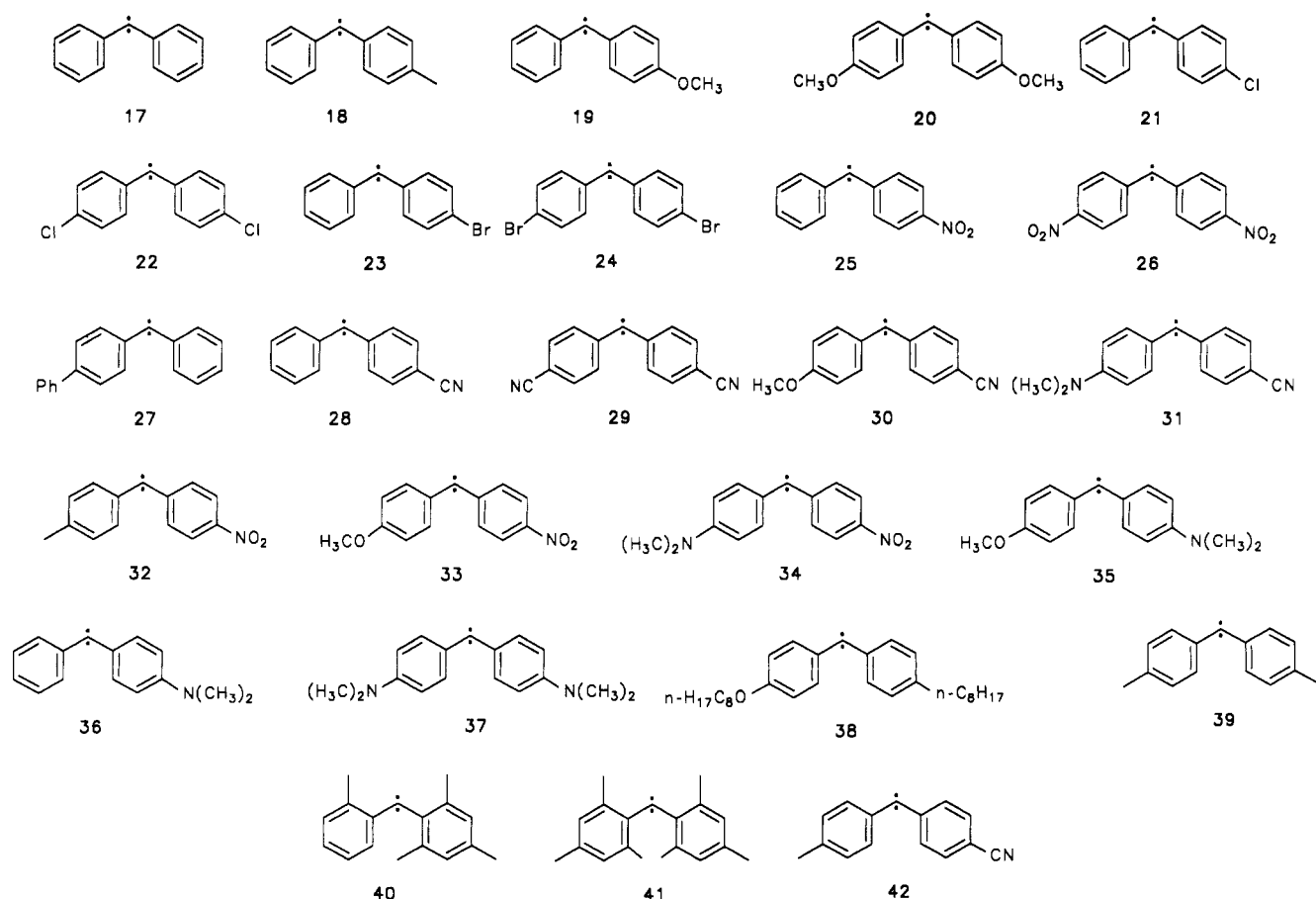
methane was shown by X-ray crystallography<sup>106</sup> to exhibit a dihedral angle between the aryl groups of 90°, which can be expected to be similar in the carbene. Another interesting observation was made by Nazran and Griller when they compared the ESR spectra of 41 before and after annealing the sample from 6 to 77 K; the shifts in the ZFS parameters are consistent with an expansion of the central C–C–C angle upon thermal relaxation of the matrix.

Iwamura et al. photolyzed polycrystalline solid samples of the diazo precursors of 19, 20, and 22.<sup>108</sup> Apart from the corresponding triplet carbenes they could also detect quintet ground state carbene pairs of 19 ( $D = 0.136 \text{ cm}^{-1}$ ;  $E = 0.013 \text{ cm}^{-1}$ ) and 20, but not of 22. The quintet carbene pair behaves magnetically like a separate molecule and is stable up to 60 K. The crucial difference between 19 and 20 on one side and 22 on the other side is found in the way the phenyl rings stagger in the corresponding diazo crystals; pseudopara orientation of the phenylmethylene substituents was observed in the diazo compounds yielding 19 and 20, whereas pseudogeminal orientation was found in the case of 22. This is exactly analogous to the situation in the case of the bis(phenylmethylene)[2.2]paracyclophanes (see section III.A.6). Ferromagnetic interaction between carbene molecules was observed by Iwamura et al. also in the case of 38.<sup>109</sup> All these examples of organic ferromagnetism are in accord with

McConnell's prediction that higher spin states should be observed where the individual paramagnetic molecules are staggered in a way that positive spin density in one molecule comes close to negative spin density in its neighbor.<sup>110</sup>

*b. UV-Vis Spectroscopy.* In 1959, DeMore, Pritchard, and Davidson published the first study intended to gain evidence for the existence of 17 in a matrix at 20 or 77 K;<sup>2</sup> however, they could observe only products of secondary carbene reactions, i.e. benzophenone and benzophenone azine (in fact, the reported absorption band at 465 nm may well have been due to 17). The emission, absorption, and excitation spectra of 17 (in 2-methyltetrahydrofuran glass) were first recorded by Gibbons and Trozzolo (Table IV).<sup>111,112</sup> They could locate the emission maximum at 480 nm; the corresponding absorption spectrum shows a  $\lambda_{\text{max}}$  at 465 nm and could additionally be derived from an excitation spectrum. The assignment to 17 was based on a correlation of the measured fluorescence intensity with the intensity of the ESR signal of 17. Gibbons and Trozzolo were able to record data for several 4-substituted diphenylcarbene derivatives (Table IV). The visible absorption of 17 was also reported independently by Moritani et al.<sup>113</sup> Closs, Hutchison, and Kohler could obtain the optical absorption spectrum of 17 in a DPE single crystal.<sup>114</sup> Utilizing linearly polarized light, they demonstrated that the transition moment of the absorption leading to photofragmentation of the diazo compound should lie along the line of the phenyl ring centers (this is in contradiction to ref 80<sup>101</sup>). The absorption and emission spectra of 17 in benzophenone crystals at extremely low temperatures were recorded by Anderson et al.,<sup>115</sup> by Graham and Lin (high-resolution absorption spectra of 17, *d*<sub>10</sub>-17, 21, and 23),<sup>116</sup> and by Sixl et al. (Table IV).<sup>96</sup> Measuring at 4.2 and 2 K, Anderson, Kohler, and Stevenson<sup>115</sup> could detect a distinct fine structure, corresponding to a zero-phonon line (470.7 nm) and its phonon sidebands. Due to large excitation–phonon coupling, the fine structure features were practically not observable at 30 K. The fluorescence lifetime and quantum yield of diphenylcarbene were recorded by Sullivan and Ware,<sup>117</sup> and in an extensive study, which also included absorption, excitation, and emission spectra of a series of its derivatives, by Ono and Ware.<sup>118</sup> The fluorescence lifetime of 17 was determined to be 123 ns in methylcyclohexane glass at 77 K, it is only slightly shortened to 73 ns by admixing ethyl iodide. 4-Substitution in all cases also led to a shortened emission lifetime, the most prominent example being the dibrominated compound 24 with  $t_{1/2} = 11.4 \text{ ns}$  (in MCH). Further detailed investigations on the fluorescence of 17 were performed by Graham and Wohler (in BZP crystal, sensitized luminescence of 17),<sup>119</sup> by Graham and Wang (influence of a magnetic field on BZP sensitized luminescence of 17),<sup>120</sup> and by Fujiwara et al.,<sup>121</sup> who compared the fluorescence maxima of diphenylcarbenes in solution at room temperature (RT), measured by laser flash photolysis (LFP), with the fluorescence maxima in low-temperature organic glasses. In the case of 17, the emission in the matrix is blue-shifted by 25 nm relative to solution phase which the authors explain in terms of matrix effects on the geometry of the carbene triplet excited state. Similar effects were found by Scaiano and Weir

Chart III



(Table IV).<sup>122</sup> As in the case of phenylcarbene, the radical cation of 17 has also been characterized. Miyazaki et al.<sup>81b</sup> irradiated diphenyldiazomethane in an *n*-butyl chloride matrix at 77 K with  $\gamma$ -rays and could observe the radical cation of the diazo compound ( $\lambda_{\text{max}} = 650$  nm), which upon irradiation yields  $17^{+\bullet}$  ( $\lambda_{\text{max}} = 390$  nm). ESR signals of the species were detected as well.

*c. Infrared Spectroscopy.* Compared to the amount of publications dealing with ESR and absorption and emission spectra of diphenylcarbene, studies employing infrared spectroscopy in noble gas or nitrogen matrices are relatively scarce. The infrared spectrum of 17 was first observed by Hess<sup>123</sup> in 1984; more recently, an extensive investigation including carbon-13 isotopic labeling has given a more complete picture about the vibrational spectrum of 17 and also allowed assignment of some of the bands.<sup>74,124</sup> The C8–C1–C2 asymmetric stretching fundamental can be assigned to a very weak band at  $1282\text{ cm}^{-1}$  ( $^{13}\text{C}$ -shift  $-24\text{ cm}^{-1}$ ), other bands exhibit only small isotopic shifts and are mainly due to vibrations of the two phenyl ring moieties.<sup>74</sup>

### 5. Other Acyclic Arylcarbenes

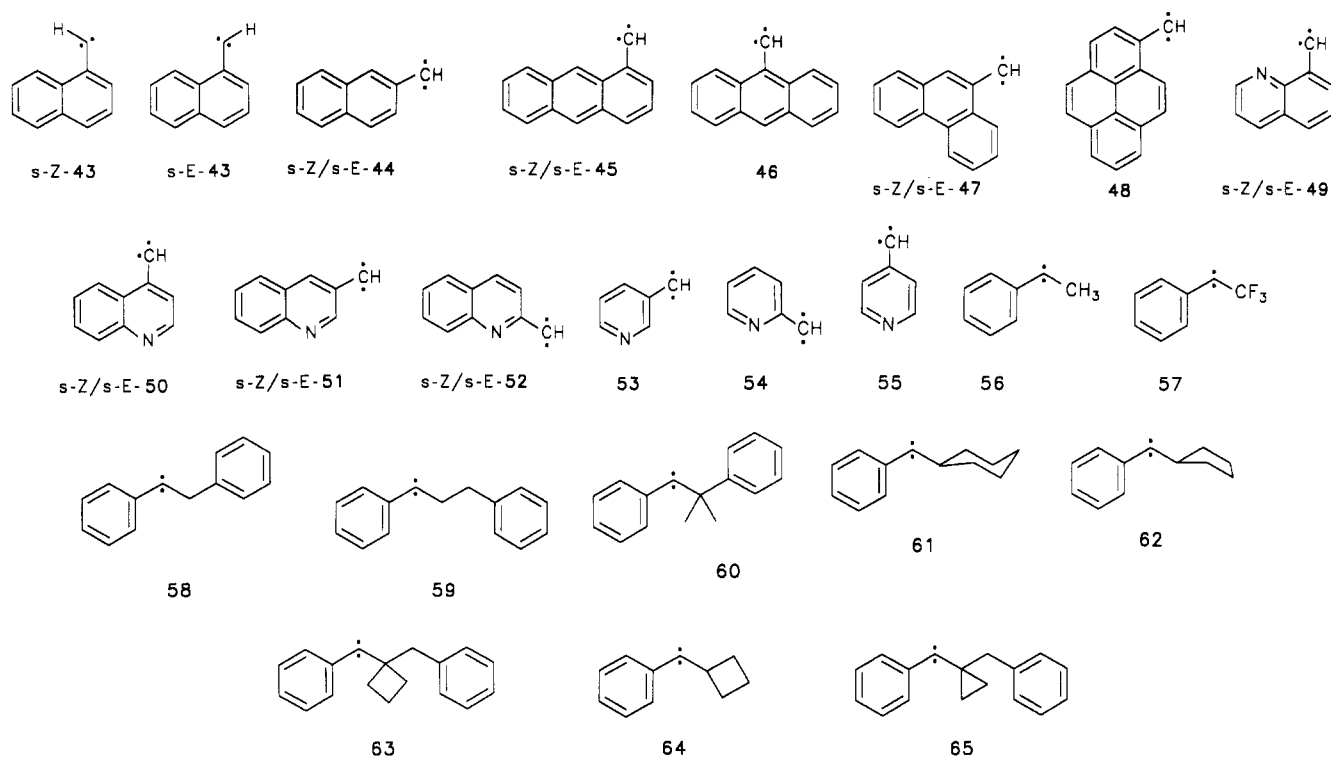
As in the case of many other carbenes, the first ESR spectrometric characterization of 1- and 2-naphthylcarbene (43 and 44, respectively, Chart IV) stems from the laboratory of Trozzolo and Wasserman.<sup>125</sup>

It is particularly interesting that in both cases a mixture of two rotational isomers, namely *s-Z* (or *syn*) and *S-E* (or *anti*), was found. The isomers could be

readily distinguished by ESR spectroscopy (Table VI); an assignment of the two triplet signals to the stereoisomers was possible. (This was confirmed later by calculations performed by Hutton and Roth.<sup>126</sup>) As expected, the *D* values are lower than in phenylcarbene. A subsequent kinetic analysis by Senthilnathan and Platz<sup>127</sup> revealed that *s-E*-43 is probably lower in energy than the *s-Z* isomer; and at the same time it is more reactive. The two observations only seem to be contradictory, they are readily explained in terms of steric interaction. Chapman et al.<sup>128a</sup> attempted to obtain optical and infrared absorption spectra of 43 and 44, but due to the lower sensitivity of absorption spectroscopy (compared to ESR spectroscopy) they were only able to observe products derived from a carbene–cyclopropene rearrangement. This work was recently continued by Albrecht and McMahon, who were able to characterize 2-naphthylcarbene (44) by IR, UV–vis, and ESR spectroscopy.<sup>128b</sup> Photolysis ( $\lambda = 560$  nm) of carbene 44 produced 2,3-benzobicyclo[4.1.0]hepta-2,4,6-triene, which in turn on shorter wavelength irradiation ( $\lambda = 290$  nm) exclusively ring opened to 44. Ring expansion to a cycloheptatetraene or rearrangement to 1-naphthylcarbene (43) was not observed.

Spectroscopic evidence for the emission spectrum of 44 was delivered by Haider, Platz, Despres, and Migirdicyan;<sup>70</sup> emission bands were observed at 569, 575, and 598 nm. If the 8-position in the naphthalene moiety of 43 is substituted by a methyl group, the carbene can no longer be observed; even at liquid helium temperature and even in the case of the deuterated

Chart IV



isotopomer, quantitative rearrangement (via a tunneling mechanism) to triplet 1,8-naphthoquinodimethane does occur.<sup>129-133</sup> It has to be noted that this extreme case of instability toward hydrogen shift is restricted to the carbene case; the corresponding nitrene was characterized via its ESR spectrum.<sup>134</sup>

Among the monoarylcabenenes which have not been discussed thus far, 1-<sup>39</sup> and 9-anthrylcarbene<sup>125</sup> (45 and 46, respectively), 9-phenanthrylcarbene (47),<sup>39</sup> and 1-pyrenylcarbene (48)<sup>127</sup> proved to be less elusive. In the case of 45 and 47 (but not in 48), where geometrical isomerism of the carbenes is to be expected, Roth and Hutton<sup>39</sup> could in fact determine the *D* values of the two isomers; they could also correlate the experimental results with calculations. An attempt to generate 4-phenanthrylcarbene remained unsuccessful.<sup>39</sup> Further work by the same group dealt with a series of quinolylcabenenes,<sup>135</sup> which are closely related to the naphthylcarbenes and which exhibit similar properties: Geometrical isomerism is observed, and spin density can be delocalized more efficiently when the carbene moiety is in 4- or 8-position (49 and 50, respectively).

The series of pyridylcarbenes constitutes a group of heteroaromatic carbenes showing great similarity to the phenylcarbene family. It was investigated by Chapman and co-workers, utilizing IR<sup>136</sup> and ESR<sup>137</sup> spectroscopy. Geometrical isomerism, although in principle to be expected in 53 and 54, was not observed. Chemical evidence for the formation of carbene 53 was provided by the formation of 3-pyridyl ketene in CO-doped Ar matrices. Irradiation ( $\lambda > 360$  nm, Ar, 10 K) of both 53 and 55 produced the same azacycloheptatetraene (183).<sup>136</sup>

In a way similar to dialkylcarbenes, most arylalkylcarbenes bearing  $\alpha$ -H atoms undergo very rapid intramolecular hydrogen shift in their singlet states to

form styrene derivatives. Thus they might seem to be rather elusive species, but obviously at cryogenic temperatures ISC is sufficiently effective in these molecules to allow the detection of their triplet ground states in matrices. The first example of this group to be discussed here, phenylmethylcarbene (phenylethylidene) (56), was first detected by Murray.<sup>77</sup> Some years later, Chapman, McMahon, and West<sup>76</sup> could obtain 56 in an Ar or Xe matrix and characterized it via ESR and IR spectroscopy. The observation, that the isomerization of 56 requires temperatures of 65 K in Xe matrix, indicates a considerable barrier to hydrogen shift imposed by spin restrictions. Due to the high dissociation energy of the C-F bond, phenyl-(trifluoromethyl)carbene 57 does not need such protection. It was characterized as a ground-state triplet molecule by means of ESR spectroscopy by Wasserman et al.<sup>63</sup> and by IR spectroscopy by Mal'tsev and co-workers.<sup>138</sup> A series of further arylalkylcarbenes, including, for example, the interesting phenylcyclopropylcarbene 65, was described in publications by Platz et al.<sup>139</sup> and by Trozzolo and Wasserman.<sup>77</sup> Platz and co-workers could not observe the parent phenylcyclopropylcarbene (ring expansion to phenylcyclobutene did occur quantitatively), but they were able to detect the benzyl-substituted derivative 65. Its ESR spectrum, and to a lesser degree those of the cyclobutyl derivatives, indicate some spin delocalization into the cyclopropane (cyclobutane) ring (relatively small *D* value).

A number of diarylcabenenes remain to be reviewed in this section.

1- and 2-naphthylphenylcarbene (66 and 67, Chart V) were examined in three studies by Fujiwara et al.,<sup>140</sup> by Maloney and Platz,<sup>141</sup> and by Migirdicyan, Platz, and co-workers.<sup>142</sup> The Japanese group was able to characterize both 66 and 67 by ESR spectroscopy, by optical absorption, and by laser-induced fluorescence.

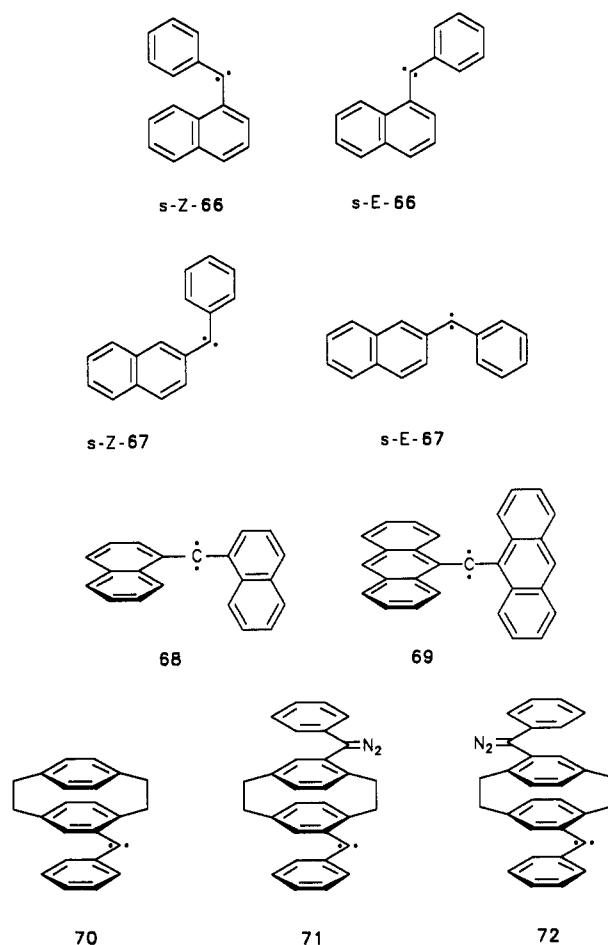
Table VI. ESR Data of Arylcarbenes (Charts IV and V)

carbene	matrix <sup>a</sup>	T, K	D/hc, cm <sup>-1</sup>	E/hc, cm <sup>-1</sup>	E/D	comments	ref
43	BZP	4,77	0.4347	0.0208	0.0478	<i>s-Z</i>	125
	MCH	6	0.4425	0.0221	0.0499	<i>s-Z</i>	135
	BZP	4,77	0.4555	0.0202	0.0443	<i>s-E</i>	125
	MCH	6	0.4629	0.0201	0.0434	<i>s-E</i>	135
44	BZP	4,77	0.4926	0.0209	0.0424	<i>s-Z</i>	125
			0.4711	0.0243	0.0516	<i>s-E</i>	
	Ar	10	0.500	0.0242	0.0484	<i>s-Z</i>	128b
			0.480	0.0277	0.0577	<i>s-E</i>	
45	b	b	0.390	b		<i>s-Z</i>	39
			0.420	b		<i>s-E</i>	
46	BZP	4,77	0.3008	0.0132	0.0439		125
47	b		0.436	b		<i>s-Z</i>	39
			0.470	b		<i>s-E</i>	
48	<i>i</i> -PrOH	77	0.40	0.019	0.0475		127
49	MCH	6	0.4434	0.0225	0.0507	<i>s-Z</i>	135
			0.4641	0.0225	0.0485	<i>s-E</i>	
50	MCH	6	0.4666	0.0219	0.0469	<i>s-Z</i>	135
			0.4865	0.0207	0.0425	<i>s-E</i>	
51	MCH	6	0.4975	0.0202	0.0406	<i>s-Z</i>	135
			0.4702	0.0245	0.0521	<i>s-E</i>	
52	pcarb <sup>c</sup>	6	0.5313	0.0246	0.0463	<i>s-Z</i>	135
			0.5038	0.0251	0.0498	<i>s-E</i>	
53	Ar	12	0.513	0.0241	0.0470		137
54	Ar	12	0.537	0.027	0.0503		137
55	Ar	12	0.533	0.0248	0.0465		137
56	Ar	10-15	0.508	0.0278	0.0547		76
	b		0.4957	0.0265	0.0535		77
57	neat	4	0.5183	0.0313	0.0604		63
58	b		0.493	0.0289	0.0588		77
59	MTHF	10	0.502	0.027	0.0538		139
60	MTHF	10	0.498	0.026	0.0522		139
71	MTHF	10	0.492	0.025	0.0508		139
62	MTHF	10	0.500	0.028	0.0560		139
63	MTHF	10	0.488	0.026	0.0533		139
64	MTHF	10	0.488	0.026	0.0533		139
65	MTHF	10	0.473	0.026	0.0550		139
66 <sup>d</sup>	MTHF	77	0.353	0.016	0.0453		140
67 <sup>d</sup>	MTHF	77	0.384	0.020	0.0521		140
67	MTHF	77	0.3898	0.0195	0.0500	<i>s-Z</i>	141
			0.4044	0.0168	0.0415	<i>s-E</i>	
68 <sup>e</sup>	MTHF	15	0.3157	0.0109	0.0345		143
68 <sup>f</sup>	MTHF	15	0.2609	0.0051	0.0195		143
69	DAK <sup>g</sup>	4-480	0.113	0.0011	0.0097		144
70	MTHF	11-50 <sup>h</sup>	0.3720	0.0161	0.0433		166
71	MTHF	11-50 <sup>h</sup>	0.3730	0.0156	0.0418		166
72	MTHF	11-50 <sup>h</sup>	0.3837	0.0168	0.0438		166

<sup>a</sup> See Table I. <sup>b</sup> Not specified. <sup>c</sup> Propylene carbonate. <sup>d</sup> The values represent the average of the two rotameric forms. <sup>e</sup> before annealing, Curie law obeyed at 15-50 K. <sup>f</sup> After annealing at 80 K. <sup>g</sup> 9,9'-Dianthryl ketone, measured at 4 K (the values represent upper limits). <sup>h</sup> Variable-temperature study.

The measurements in the UV-vis range unveiled a long wavelength absorption ranging up to 600 nm and a corresponding emission in the region 575-700 nm, with maxima at 598 (66) and 584 nm (67). The emission is quite short-lived in both cases (10 and 17 ns in 66 and 67, respectively). The ESR spectra obtained by Fujiwara et al. point to a high degree of spin delocalization within the aromatic system. Geometrical isomerism is to be expected in both compounds, but the Japanese authors did not try to further resolve the spectra, which was then done for 67 by Maloney and Platz.<sup>141</sup> In a subsequent joint effort of Platz's team in Ohio with Migirdicyan's group in Paris, temperature, magnetic field, and concentration effects on the fluorescence behavior of 66 and 67 were examined in considerable detail.<sup>142</sup> One of the interesting results: The emission spectra of both carbenes are dictated to a large extent by the naphthalene moiety. For example, the vibrational fine structure in the fluorescence spectrum of 67 can be analyzed very conveniently in terms of the normal modes of the naphthalene molecule. The emission

Chart V



spectra of both carbenes consist of broad and sharp bands, the relative intensity of which depend critically on sample concentration, temperature, and irradiation duration; i.e., on sample history. Di-1-naphthylcarbene (68) was subject of work published by Tukada, Iwamura, and coworkers.<sup>143</sup> Its ESR spectrum, measured at 15 K, is very typical for a bent carbene molecule with extensive spin delocalization. Upon annealing, however, geometrical relaxation takes place (a similar effect was reported by Griller et al. in the case of dimesitylcarbene), and the carbene assumes a linear structure, as shown by the ZFS parameters. This change is irreversible, recooling does not build up the first signal again.

9,9'-Dianthrylcarbene (69) is a sterically highly hindered molecule which exhibits many unusual properties. Its chemistry was examined by ESR spectroscopy by Wasserman et al.<sup>144</sup> and by optical absorption spectroscopy in matrix as well as by a number of time-resolved techniques in solution by Griller and coworkers.<sup>145</sup> In solution, it reacts with <sup>3</sup>O<sub>2</sub> nearly 5 orders of magnitude slower than all other triplet carbenes, and the main mode of decay is self-quenching, which is diffusion controlled, in spite of the bulky molecular framework. In an anthracene matrix, it can be detected at temperatures as high as 160 °C! The reason for all this exotic behavior is found in its linear geometry and, therefore, in the fact that the spin density is nearly completely delocalized within the molecule. The ZFS parameters given in Table VI were measured at 4 K and represent the upper limits; at higher temperatures,

$E$  is virtually zero.<sup>144</sup> Finally, the UV spectrum of 69, matrix-isolated in isopentane/ether, shows two maxima at 355 and 445 nm.<sup>145</sup>

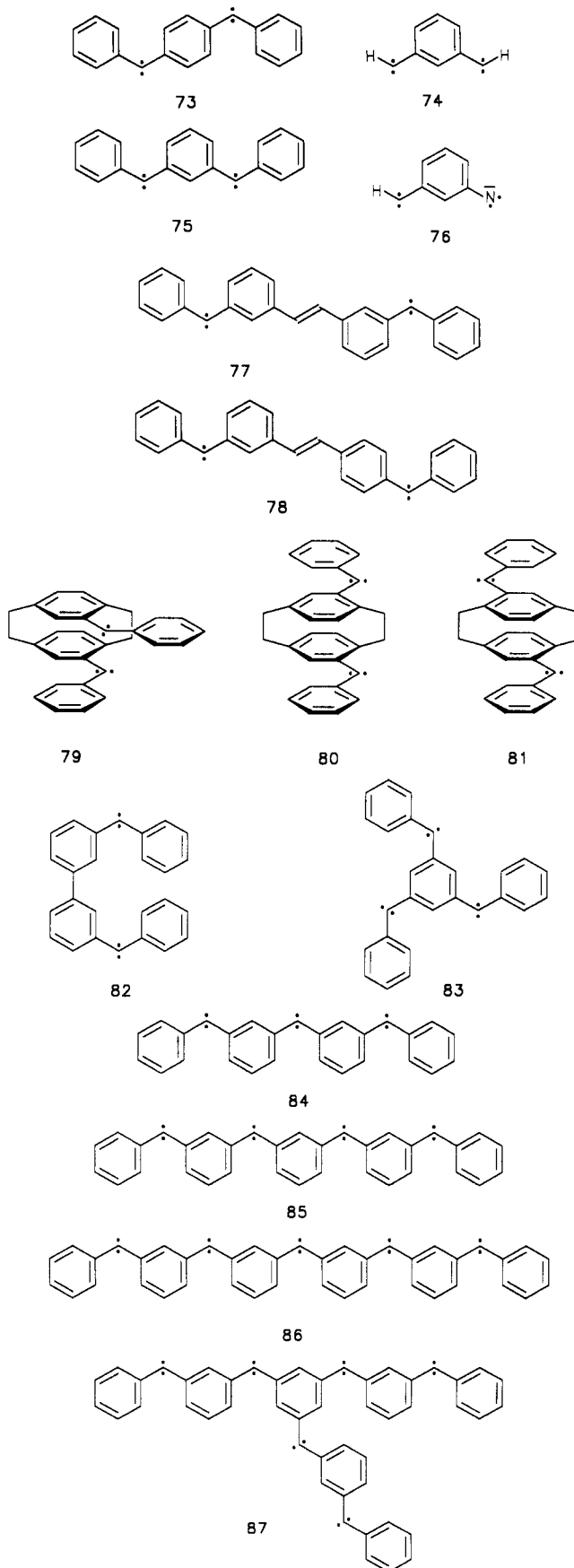
### 6. Di-, Oligo-, and Polyarylcabenenes

One of the topics of current interest in carbene research is the generation of molecules with a large number of carbene "functional groups". The aim is to achieve ground-state spin multiplicities as high as possible and thus to approach organic para- and ferromagnetism. Because of possible technical applications this field is of high interest and has been reviewed several times.<sup>19,77,82,146-148</sup> The first dicarbene reported in the literature dates from 1963, when the generation of *p*-phenylene bis(phenylcarbene) (73, Chart VI) was published by Trozzolo et al.<sup>149</sup> It turned out to be a nearly linear ground-state triplet molecule with extensive spin delocalization, which is best described in terms of a *p*-benzoquinodimethane diyl type structure (Table VII). A later study, performed by Sixl et al.,<sup>96</sup> yielded a somewhat more complicated picture of the chemistry of 73 and its diazo precursor, including a highly labile monodiazomonomocarbene intermediate, which splits off the second molecule N<sub>2</sub> thermally with a very low activation energy.

During the last two decades, research activities on di- and oligocabenenes have focused on compounds with *m*-phenylene-bridged carbene centers, as this class of carbenes is promising for the generation of organic high-spin molecules. Applying Longuet-Higgins' theory,<sup>150</sup> in 1963 Trozzolo et al. calculated that *m*-phenylene biscabenenes 74 and 75 should have quintet ground states;<sup>149</sup> the ZFS parameters were published two years later by Wasserman et al.<sup>151</sup> and, independently, by Itoh (Table VII).<sup>152</sup> A closely related compound is the mixed carbene-nitrene derivative, (3-nitrenophenyl)-carbene (76), which was reported by Tukada, Mutai, and Iwamura.<sup>153</sup> It also has a quintet ground state; the  $D$  value lies almost exactly between those of 74 and *m*-phenylenedinitrene.<sup>151</sup> A more exotic species, the radical anion of 75, may also be mentioned at this place; it was generated by successive  $\gamma$ -irradiation and visible irradiation of the diazo compound, and it proved to have a doublet ground state (the quartet excited state is very easily accessible).<sup>154</sup>

The concept of linking carbene centers by *m*-phenylene bridges was further extended by Japanese researchers; subsequently, septet,<sup>155,156</sup> nonet,<sup>156-160</sup> undecet,<sup>161</sup> and very recently the world-record tridecet<sup>162</sup> spin multiplicities could be achieved. Two different types of carbene arrangements were utilized: One-dimensional chains as in 84-86, and two-dimensional networks as in 87 and, in its elementary form, 83. The most thoroughly examined example of this group of high-spin molecules is the nonet tetracarbene 85, which was investigated in a series of elaborate studies by the group centered around Iwamura. The system was surveyed by means of ESR spectroscopy (Table VII)<sup>157,158</sup> and by measuring the paramagnetic susceptibility;<sup>159,160</sup> the results show that it exhibits a number of quite interesting features, among them conformational changes upon annealing (as indicated by the ESR spectra), a single-photon photodissociation of the tetradiazo compound to the tetracarbene, the onset of antiferromagnetic intermolecular interactions below 65 K when

Chart VI



measured in MTHF glass, and a large saturation effect on the magnetization of 85, if a strong external magnetic field is applied at low temperatures (Table VII). By comparing the magnetic behavior of 85 with that of



Table VII. ESR Data of Di- and Oligocarbenes (Chart VI)

carbene	matrix <sup>a</sup>	T, K	multi- plicity <sup>b</sup>	D/hc, cm <sup>-1</sup>	E/hc, cm <sup>-1</sup>	E/D	ref
73	DBB <sup>c</sup>	77	T	0.0521	<0.002	<0.03839	149
	BZP	180	T	0.065	0.005	0.07692	96
74	d		Q	0.0844	0.0233	0.2761	151
75	d		Q	0.0701	0.020	0.2853	151
	BZP	77	Q	0.07131	0.01902	0.2667	152
75	MTHF	3.1-77	D <sup>e</sup>				154
	MTHF	3.1-77	quartet <sup>e,f</sup>	0.1200	0.0045	0.0375	154
76	MTHF	18	Q	0.124	0.002	0.0161	153
77	MTHF	16-65	S				163
	MTHF	16-65	Q <sup>g</sup>				163
78	MTHF	16-65	Q				163
79	MTHF	11	Q	0.0624	0.0190	0.3045	166
	MTHF	11	T <sup>h</sup>	0.1872	0.0570	0.3098	166
80	MTHF	11	S				166
	MTHF	11	T <sup>h</sup>	0.1840	0.0023	0.0125	166
81	MTHF	11	Q	0.1215	0.0085	0.06996	166
82	BZP	4.2	S				165
	BZP	4.2	T <sup>i,j,k</sup>	0.29583	0.06032	0.2039	165
	BZP	4.2	Q <sup>i,j,k</sup>	0.10349	0.01457	0.1408	165
	BZP	4.2	T <sup>i,j,k</sup>	0.23895	0.06452	0.2700	165
	BZP	4.2	Q <sup>i,j,k</sup>	0.08329	0.02114	0.2538	165
83	DBB <sup>g</sup>	4.2	septet	0.04158	0.01026	0.2468	155
84	BZP	77	septet	0.06670	0.00045	0.00675	156
85	BZP	1.8-56	nonet	0.03161	0.00394	0.1246	158
86	TBB <sup>i</sup>	77	undecet	0.0168	0.0036	0.2143	161
87	MTHF	10	tridecet				162

<sup>a</sup> See Table I. <sup>b</sup> Ground-state multiplicity (if not stated otherwise); S, singlet; D, doublet; T, triplet; Q, quintet. <sup>c</sup> 1,4-Dibenzoylbenzene. <sup>d</sup> Not specified. <sup>e</sup> Radical anion. <sup>f</sup> Excited-state multiplicity. <sup>g</sup> 1,3-Dibenzoylbenzene. <sup>h</sup> Low-temperature form. <sup>i</sup> The singlet, triplet, and quintet states are nearly degenerate. <sup>k</sup> High-temperature form. <sup>j</sup> 1,3,5-Tribenzoylbenzene.

comparable metal particles with less than 30-Å diameter, the authors came to the conclusion that 85 does not behave like a molecular ferromagnet, but rather like a molecular superparamagnet.<sup>160</sup> Similar properties have been found recently in the case of the tridecet hexacarbene 87.<sup>162</sup>

The game of connecting carbene subunits to complicated oligomeric structures has also been played with linking units other than *m*- or *p*-phenylene bridges. Examples are ethylene-bridged compounds such as 77 and 78 and the 3,3'-biphenyl-bridged molecule 82. 77 and 78 were described by Murata, Sugawara, and Iwamura;<sup>163</sup> the meta,meta' isomer 77, which has to be labeled "disjoint" according to the theory of Borden and Davidson<sup>164</sup> has a singlet ground state, the quintet (and probably also the triplet) state is thermally accessible at 50 K. The meta,para' isomer 78 ("non-disjoint"), on the other hand, is expected to have a quintet ground state, which is confirmed by the experiment. Compound 82 was examined by Itoh.<sup>165</sup> In this case, the singlet (which is the ground state), triplet, and quintet states are almost degenerate; the most significant effect of temperature on the ESR spectra is observed at 140 K, when an irreversible change in conformation takes place.

A completely different approach to induce paramagnetic interaction between carbene molecules can be achieved by stacking the phenyl rings of the carbene units in such a way that positive spin density in one molecule comes close to negative spin density in its neighbor, according to McConnell's relationship,<sup>110</sup> which is observed for example in partially irradiated crystals of some diphenyldiazomethane derivatives.<sup>108,109</sup> (See section III.A.4.) A more systematic exploration of

this type of carbene interaction was published by Izuoka et al.,<sup>166</sup> who incorporated two carbene units into a [2.2]paracyclophane skeleton, so that both phenyl rings were connected to only one divalent carbon atom. The resulting relative orientations of the carbene centers are labeled pseudo ortho as in 79 and pseudometa or pseudopara as in 80 or 81, respectively (Table VII). As expected according to theory, 79 and 81 show paramagnetic behavior with quintet ground states (a triplet state is thermally accessible in 79), whereas in 80 the two diphenylcarbene subsystems interact in an anti-ferromagnetic fashion (again, a triplet excited state may be populated thermally). As byproducts, monodiazomonomocarbenes were also characterized by ESR spectroscopy (Table VI). The spin densities in 79-81 were subject of a recent theoretical study by Sinha and Ramasesha.<sup>167</sup>

## 7. Vinyl- and Ethynylcarbenes

The vinylcarbene-cyclopropene rearrangement is of considerable interest in preparative organic chemistry<sup>168</sup> and therefore this reaction has been studied in some detail.<sup>169-172</sup>

Photolysis of vinyldiazomethane in a variety of organic glasses at 6 K produced vinylcarbene (88, Chart VII) in its triplet ground state.<sup>39,173</sup> Two distinct ESR spectra were recorded and assigned to a pair of geometric isomers with the hydrogen at the carbene center in *s-Z* and *s-E* position (Table VIII). The assignment is based on a simple point spin model,<sup>126</sup> from which a lower *D* value for the *s-E* rotamer is calculated. In the range 6-15 K the Curie law is obeyed, as it is required for triplet ground-state species.

The *s-Z/s-E* ratio varies between 0.65 and 0.05, depending on the matrix, temperature, and irradiation time. From the *E/D* ratio the H-C-C bond angle at the carbene center is estimated to 140°.<sup>173</sup>

The spin density on C-1 was estimated by comparison of the average *D* value of *s-E* and (*s-Z*)-vinylcarbene

Chart VII

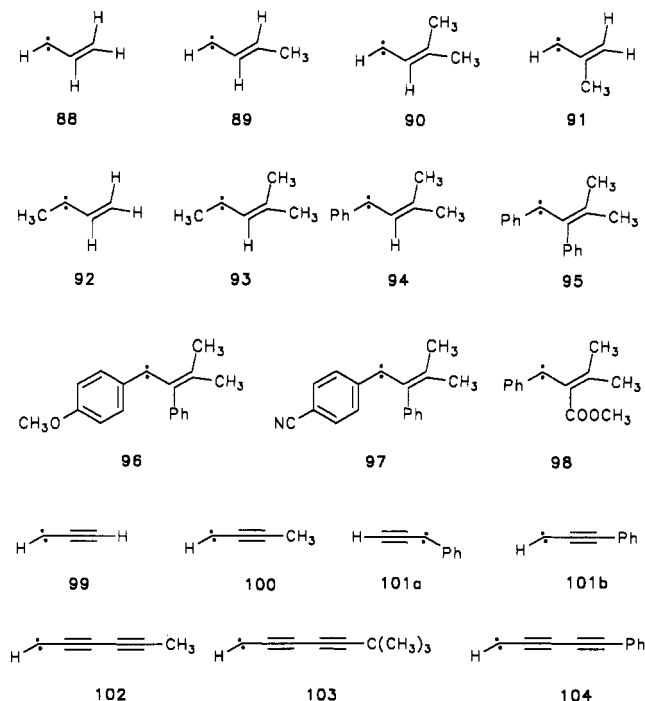
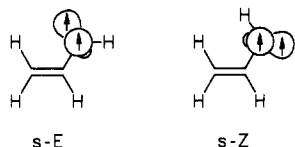


Table VIII. ESR Data of Vinyl- and Ethynylcarbenes (Chart VII)

carbene	matrix <sup>a</sup>	T, K	D/hc, cm <sup>-1</sup>	E/hc, cm <sup>-1</sup>	E/D	comments	ref
88	MTHF	6	0.4093	0.0224	0.0547	<i>s-E</i>	173
			0.4578	0.0193	0.0422	<i>s-Z</i>	
89	neat	<i>b</i>	0.4078	0.0233	0.0571	<i>s-E</i>	39
			0.4574	0.0208	0.0455	<i>s-Z</i>	
90	neat	<i>b</i>	0.4124	0.0237	0.0575	<i>s-E</i>	39
			0.4538	0.0202	0.0445	<i>s-Z</i>	
91	neat	<i>b</i>	0.4009	0.0249	0.0621	<i>s-E</i>	39
			0.4310	0.0249	0.0578	<i>s-Z</i>	
92	neat	<i>b</i>	0.3990	0.0220	0.0551	<i>s-E</i>	39
			0.4531	0.0200	0.0441	<i>s-Z</i>	
93	neat	<i>b</i>	0.4002	0.0220	0.0550	<i>s-E</i>	39
			0.4421	0.0234	0.0529	<i>s-Z</i>	
94	neat	<i>b</i>	0.357	0.0194	0.0543	<i>s-Z</i>	39
95	MCH/IP (4:1)	5	0.3580	0.0206	0.0575		175
96	MCH/IP (4:1)	5	0.3336	0.0179	0.0537		176
97	MCH/IP (4:1)	5	0.3368	0.0182	0.0540		176
98	MCH/IP (4:1)	5	0.3643	0.0166	0.0456		175
99	PCTFE	77	0.6276	0.0	0.0		177
100	PCTFE	77	0.6263	0.0	0.0		177
101	PCTFE	77	0.5413	0.0035	0.00647		177
102	PCTFE	77	0.6087	0.0	0.0		177
103	PCTFE	77	0.6055	0.0	0.0		177
104	PCTFE	77	0.5530	0.0	0.0		177

<sup>a</sup> See Table I. <sup>b</sup> Not specified.

with that of CH<sub>2</sub> (Table VIII) to 0.58.<sup>39,173</sup> Thus the delocalization of the unpaired electron in the  $\pi$ -system is similar to that of the allyl radical, while the second unpaired electron is localized in a  $\sigma$ -orbital at C-1.

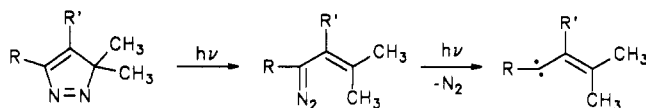
Both rotamers are stable below 15 K but rapidly react to form products of unknown constitution at 77 K.<sup>173</sup> At temperatures between 20 and 35 K, 88 decays with  $E_a < 200$  cal/mol, the *s-E* isomer decays somewhat faster than the *s-Z* isomer. At temperatures far below the melting point of the matrix, diffusion processes are expected to be very slow, and thus intramolecular rather than intermolecular processes—presumably via ISC to the singlet surface—are responsible for the decay of 88. A likely intramolecular reaction is ring closure to cyclopropene.

Methyl-substituted vinylcarbenes 89–93, generated by irradiation of substituted diazopropenes in frozen solution, exhibit the same type of geometric isomerism as 88, while for 94, with a phenyl group at the carbene center, only one isomer was observed.<sup>39</sup>

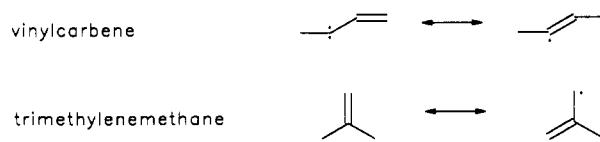
Chapman described the selective formation of the *s-E* and *s-Z* conformers of 88, characterized by IR and ESR spectroscopy, by irradiation of the corresponding rotamers of diazopropene in inert gas matrices.<sup>174</sup> UV irradiation ( $\lambda > 340$  nm) produced cyclopropene, allene, and methylacetylene as the major products.

Arnold et al. generated a series of vinylcarbenes 95–98 with aryl substituents at the carbene center by irradiation of 3*H*-pyrazoles or vinyl diazomethanes in organic glasses at 5 K (Table VIII).<sup>175,176</sup> The vinyl diazomethanes were synthesized by irradiation of 3*H*-pyrazoles in solution at 10 °C and are stable at room temperature for several hours. The stereochemistry of the pyrazoles or vinyl diazomethanes is presumably

preserved upon irradiation, which rationalizes that only the *s-E* rotamers of vinylcarbenes 95–98 were detected.



Curie law dependence was observed between 5 and 45 K, which proves the triplet ground state of these carbenes. The *D* values correspond to a mean separation of the unpaired electrons of approximately 2 Å, indicating a higher degree of localization than in trimethylenemethanes.



Irradiation of the cyclopropene corresponding to 95 did not produce the carbene or other triplet species,<sup>176</sup> which was explained by the low rate of ISC in the cyclopropenes and by the observation that triplet cyclopropenes do not ring open in other systems.<sup>176</sup>

Bernheim et al.<sup>177</sup> generated propargylene 99 and several of its derivatives 100–104 by irradiation of the corresponding ethynyl diazo compounds with the Pyrex-filtered light of a mercury arc lamp in poly(chlorotrifluoroethylene) at 77 K. Characterization of the carbenes by ESR spectroscopy allowed the authors to draw some conclusions about the electronic structure of propargylenes. For all derivatives—except phenylpropargylene (101)—an *E* value of zero was determined. The explanation of this was that 99 and its derivatives are linear (but see discussion below), and thus the  $\pi$ -system can be interpreted as a superposition of two linear allyl radical  $\pi$ -electron structures. In 101 the delocalization of spin density is expanded over the phenyl  $\pi$ -system, and therefore a measurable value for *E* is observed. The delocalization is also reflected in

a lower  $D$  value—a consequence of the larger mean distance of the unpaired electrons—for the phenyl-substituted derivatives compared to the parent carbene **99**.

Infrared spectra of propargylene and partially deuterated isotopomers were reported by Chi and Leroy,<sup>178</sup> who prepared the carbenes by irradiation ( $\lambda > 350$  nm) of diazopropyne, matrix isolated in krypton at 30 K. IR absorptions at 3285, 2140, 408, and 259  $\text{cm}^{-1}$  were assigned to fundamental vibrations of **99**. Only one C–H stretching frequency was observed, which implies that both H-atoms are equivalent, and thus a linear structure was deduced from the IR data. Some evidence for the formation of **99** by vacuum ultraviolet photolysis of propyne in Ar at 14 K was given by Jacox and Milligan.<sup>179</sup>

Maier et al. generated **99**,  $d_1$ -**99**, and  $d_2$ -**99** by photolysis of diazopropyne as well as cyclopropenylidene in Ar at 12 K.<sup>180,181</sup> Fundamental vibrations were now assigned to absorptions at 3265.5 (s), 1620.0 (vw), 550.4 (m), 401.6 (m), and 245.9 (s)  $\text{cm}^{-1}$ , in agreement with high-level *ab initio* calculations. (The 2140- $\text{cm}^{-1}$  absorption described by Chi and Leroy<sup>178</sup> is obviously due to a contamination, the isomeric vinylidenecarbene (**192**) exhibits the antisymmetric C=C vibration around 1950  $\text{cm}^{-1}$ .) The calculations also show that propargylene is a nonrigid molecule, and the anharmonicity of the potential surface has to be taken into account to reproduce IR frequencies and especially intensities. The nonrigidity is caused by a very low lying transition state (0.09 kcal/mol according to MP4/6-311++G(df,pd) calculations by DeFrees and McLean<sup>182</sup>) which separates the two degenerate bent structures. Thus the matrix IR data provide experimental evidence for the calculated structures.

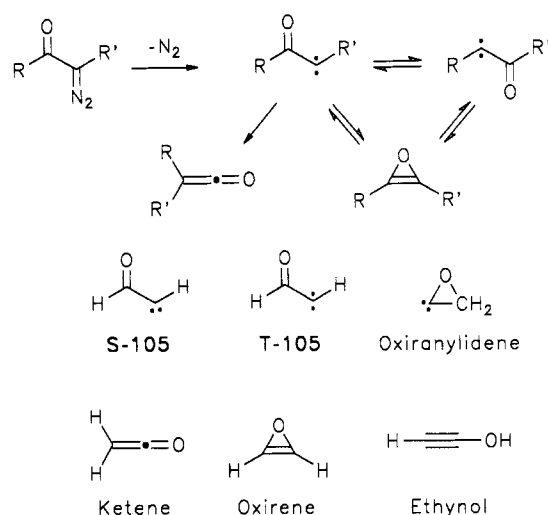
Propargylene **99** was formed in a photostationary equilibrium with vinylidenecarbene **192** and cyclopropenylidene **132** (Scheme VIII).<sup>180,181</sup> Irradiation at 313 nm produces high yields of vinylidenecarbene (**192**) and small amounts of cyclopropenylidene (**132**), and at 254-nm irradiation **192** again rearranges to **99**.

IR, UV-vis, and ESR spectra of phenylpropargylene (**101**) were recently reported by DePinto and McMahon.<sup>183</sup> Photolysis of 1-phenyldiazopropyne in Ar at 10 K produced 1-phenylpropynylidene (**101a**) as the only major photoproduct. Warming the matrix to 37 K resulted in the disappearance of **101a** and in the formation of its isomeric 3-phenylpropynylidene (**101b**). The spectra were assigned by using  $^{13}\text{C}$ -labeling, and from the ESR hyperfine splittings bond angles at the carbene carbon atoms of 158–160° and 157–158° were calculated for **101a** and **101b**, respectively.

## B. $\alpha$ -Carbonylcarbenes

$\alpha$ -Carbonylcarbenes are of considerable interest as intermediates in the Wolff rearrangement.<sup>19</sup> There has been some discussion whether singlet ketocarbenes are energy minima on the hypersurface, or loss of nitrogen in the diazo precursor and rearrangement are concerted reactions. As a result of *ab initio* calculations Nguyen et al. propose that during the retro-Wolff-type rearrangement of a diazafulvenone to cyanovinyl isocyanate the singlet ketocarbene is not a distinct intermediate.<sup>185</sup> The isolation of triplet ketocarbenes in low-temperature

Scheme III



matrices, however, suggests that at least in some cases the singlets are long lived enough at low temperature for ISC to occur (Scheme III). The alternative route to triplet ketocarbenes is ISC of excited diazo precursors with subsequent spin-allowed cleavage to produce the triplet carbenes.

Another point of interest is the oxirene system, which is a potential intermediate in the ketocarbene–ketene rearrangement. Matrix isolation spectroscopy is the method of choice to shed some light on these rather complicated processes.

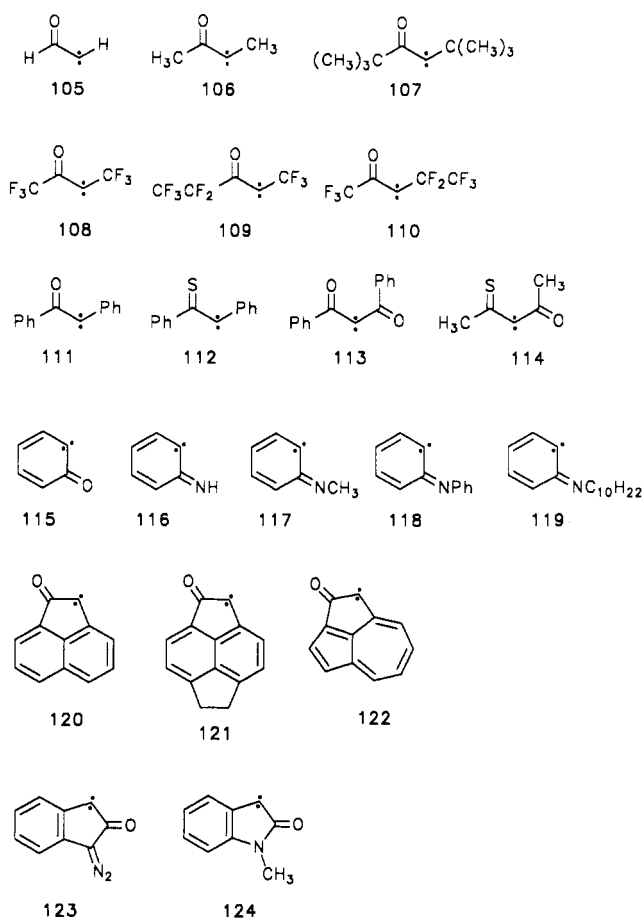
### 1. Ketocarbenes

ESR spectra of several ketocarbenes and related compounds have been published during the last two decades (Table IX),<sup>184</sup> but other spectroscopic data are quite sparse. This is mainly due to the Wolff rearrangement, which prevents the buildup of the high concentrations of carbenes necessary for IR or UV-vis work.

Formylcarbene (**105**, Chart VIII), the parent compound of ketocarbenes, has not yet been characterized experimentally. Several *ab initio* calculations on **105** and other  $\text{C}_2\text{H}_2\text{O}$  isomers have been published.<sup>186–190</sup> Tanaka and Yoshimine found by using CI calculations with a double- $\zeta$  basis on the singlet  $\text{C}_2\text{H}_2\text{O}$  surface that ethynol is less stable by 36 kcal/mol than ketene, but separated by a 73 kcal/mol barrier.<sup>187</sup> Oxirene is 82 kcal/mol less stable than ketene, with a barrier for the oxirene–formylcarbene rearrangement of only 2 kcal/mol. An important conclusion concerning matrix isolation is that formylcarbene is unstable with respect to the rearrangement to ketene.

The role of triplet and diradical-like singlet  $\text{C}_2\text{H}_2\text{O}$  molecules in the Wolff rearrangement was explored by Novoa et al.<sup>189</sup> According to MC-SCF 6-31G(d) calculations singlet **105** is 1.3 kcal/mol less stable and (singlet) oxirene 4.2 kcal/mol more stable than the triplet carbene. In contrast to other *ab initio* calculations, the MC-SCF calculations predict the singlet formylcarbene to be a planar diradical with a slightly lower lying triplet. The (singlet) formylmethylene to oxirene transition state lies only 2.9 kcal/mol above triplet **105**, and thus even under the conditions of low-temperature matrix isolation, isomerization of the triplet carbene to oxirene would be facile.

## Chart VIII



Hochstrasser and Wirz reported the synthesis of ethynol in Ar matrices by UV irradiation of ketene<sup>191</sup> or 3-hydroxycyclobutene-1,2-dione.<sup>192</sup> Short wavelength UV irradiation ( $\lambda \leq 248$  nm) of ethynol produces ketene; other  $\text{C}_2\text{H}_2\text{O}$  intermediates such as oxirene, formylcarbene, or oxiranylidene were not observed by IR spectroscopy.

Maier et al. undertook a systematic study of the matrix photochemistry of a variety of diazoketones which under "ordinary conditions" in solution have only a small tendency for Wolff rearrangement.<sup>193</sup> Perfluorinated diazoketones and diazoketones with bulky substituents should be especially suitable for the generation of ketocarbenes and oxirenes in low-temperature matrices, but in all cases ketenes were the principal products of matrix photochemistry. Attempts to generate oxirenes via photochemical cycloreversion reactions in low-temperature matrices also failed.<sup>194</sup>

ESR spectroscopy allows detection of triplet ketocarbenes, even if the yield is very low. Strausz et al. succeeded in recording the ESR spectrum of pivaloyl-*tert*-butylcarbene (107) in a polycrystalline powder sample or organic glass (MCH/isopentane 4:1) at 22 K (Table IX). Irradiation ( $\lambda > 300$  nm) of 2,2,5,5-tetramethyl-4-diazo-3-hexanone produced ESR signals which were stable for hours at temperatures below 50 K and decayed with first-order kinetics above 80 K.<sup>195</sup> The triplet spectrum was assigned to the *s-E* rotamer.

In contrast to 107, acetylmethylcarbene (106) could not be detected by ESR spectroscopy under similar conditions.<sup>195</sup> This is in accordance with the observation that irradiation of 3-diazo-2-butanone in Ar matrices

at 10 K produces both dimethyl ketene (product of Wolff rearrangement) and methyl vinyl ketone (product of 1,2-H shift).<sup>196</sup> The diazo ketone exists as a mixture of conformers and it was proposed that the *s-E* rotamer leads preferentially to the ketone and the *s-Z* rotamer to the ketene (Scheme IV).

The matrix photochemistry of 3-diazo-2-butanone was recently reinvestigated by Bodot et al.<sup>197</sup> The major photoproducts were, as described in a previous study by Strausz et al.,<sup>196</sup> dimethyl ketene and methyl vinyl ketone. *s-Z* and *s-E* rotamers of the latter were identified by comparison with the authentic matrix-isolated ketone. A minor product with a  $\text{C}=\text{C}$  stretching vibration at  $2137\text{ cm}^{-1}$  was claimed to be 1,2-dimethyloxirene, which was rationalized by comparison with *ab initio* calculations. The thermal isomerization of the oxirene to the corresponding ketene was observed at temperatures as low as 25 K, suggesting a barrier of activation below 2 kcal/mol.<sup>197b</sup> Some evidence for the formation of ketocarbene 106 was also presented, and IR bands of very low intensity at 1096, 1032, 1028, and  $758\text{ cm}^{-1}$  were tentatively assigned to *d*<sub>6</sub>-106.<sup>197a</sup> In 1% or 5% CO-doped krypton matrices 106 was trapped presumably as methyl acetyl ketene. (Several IR absorptions were assigned to the ketene.)

Perfluoroacetylmethylcarbene (108) was characterized by ESR spectroscopy in organic glasses or as powder sample at 11 K (Table IX).<sup>198</sup> Two rotamers, *s-Z* and *s-E*, were formed in a ratio of 9:1 as primary products on irradiation of the diazo precursor. Both rotamers are stable below 50 K and the Curie law is obeyed in the range 8–50 K, indicating ground-state triplet molecules. At higher temperatures the *s-E* conformer is thermally less stable than the *s-Z* conformer. The latter decays at temperatures above 100 K with good first-order kinetics and the activation parameters were determined from the Arrhenius plots to  $E_a = 5.0 \pm 0.5$  kcal/mol and  $\log A = 6.5 \pm 0.9$ .<sup>198</sup> From the low value of the preexponential factor it was concluded that ISC to singlet 108 is rate determining for the Wolff rearrangement. The rotamers do not interconvert thermally or photochemically, which suggests that the barrier of rotation is higher than the barrier of the Wolff rearrangement. The characterization of 108 by IR spectroscopy in an Ar matrix has also been claimed,<sup>199</sup> but later it was shown that neither carbene 108 nor the corresponding oxirene were produced in amounts which allow IR detection.<sup>200</sup>

Other perfluorinated ketocarbenes which were characterized by ESR spectroscopy are 109 and 110 (Table IX).<sup>201</sup> Again, rotational isomers *s-Z* and *s-E* were observed, with *s-Z* being formed in higher yield and being thermally more stable than *s-E*. In Ar matrices at 10 K the ketocarbenes 109 and 110 could not be observed.

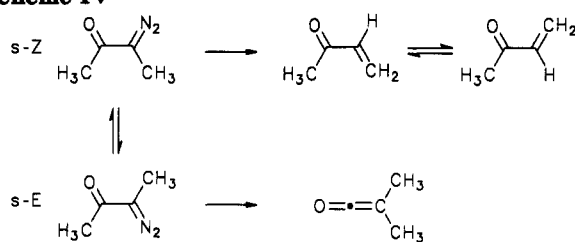
Several benzoylcarbenes have been characterized by matrix ESR spectroscopy. Benzoylphenylcarbene (111) was generated by irradiation ( $\lambda > 345$  nm) of azibenzil in organic glasses or as powder at 77 K.<sup>31,82,202</sup> The ESR spectra reveal the formation of both the *s-Z* and *s-E* rotamers, which were assigned according to their ZFS parameters (Table IX).<sup>202</sup> The *s-Z* rotamer is the major product (>90%) and a thermal interconversion of *s-Z* and *s-E* is not observed (Scheme V). The activation barriers for the thermal decay at temperatures above

Table IX. ESR Data of Ketocarbenes (Chart VIII)

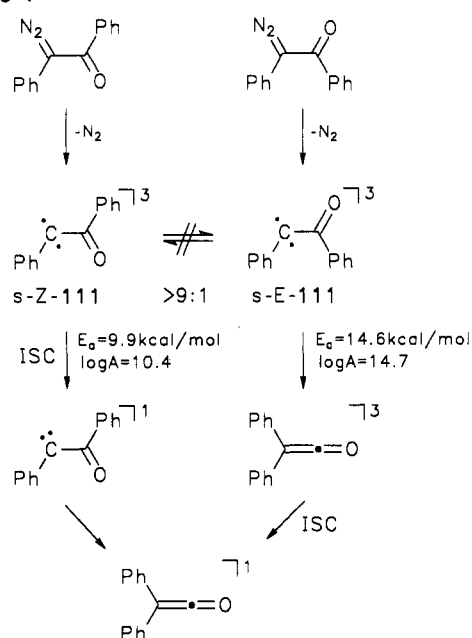
carbene	matrix <sup>a</sup>	T, K	D/hc, cm <sup>-1</sup>	E/hc, cm <sup>-1</sup>	E/D	comments	ref
107	MCH/IP (4:1)	22	0.493	0.077	0.1562	stable at 50 K	195
	neat	22	0.500	0.074	0.148		
108	neat	11	0.605	0.034	0.0562	<i>s-E</i>	198
			0.572	0.079	0.1381	<i>s-Z</i>	
109	neat	10	0.563	0.080	0.1421	<i>s-E</i>	201
			0.564	0.039	0.0691	<i>s-Z</i>	
110	neat	10	0.553	0.091	0.1646	<i>s-E</i>	201
			0.558	0.029	0.0520	<i>s-Z</i>	
111	neat	77	0.3123	0.0519	0.1662	<i>s-E</i>	202
			0.3916	0.0518	0.1323	<i>s-Z</i>	
112	neat	77	0.0318	0.00105	0.0330	stable at 77 K	223
113	neat	77	0.0801	0.0232	0.2896	<i>s-Z,s-E</i>	204
			0.029	<i>b</i>	<i>s-E,s-E</i>		
116	neat	77	0.1704	0.0025	0.0150	stable at 77 K	206
117	neat	77	0.146	<i>b</i>			206
118	neat	77	0.1150	0.0037	0.0322	<i>s-E</i>	206
			0.1054	0.0029	0.0275	<i>s-Z</i>	
119	<i>b</i>	<i>b</i>	0.13	0.004	0.0308		206
120	Ar	15	0.406	0.0264	0.0650		208
121	Ar	15	0.401	0.0253	0.0631		208
122	Ar	15	0.427	0.0179	0.0419		208
123	Ar	10	0.3631	0.0225	0.0620		209
124	HFB	4	0.38				211

<sup>a</sup> See Table I. <sup>b</sup> Not specified.

## Scheme IV



## Scheme V



150 K (*s-Z*) and 170 K (*s-E*) were determined to  $E_a = 9.9$  kcal/mol,  $\log A = 10.4$  and  $E_a = 14.6$  kcal/mol,  $\log A = 14.7$ , for *s-Z* and *s-E*, respectively.<sup>202</sup> Thus the *s-Z* rotamer is less stable than the *s-E* rotamer, and the large difference in the Arrhenius preexponential factors indicates different mechanisms for the decay. A possible explanation is the adiabatic isomerization to

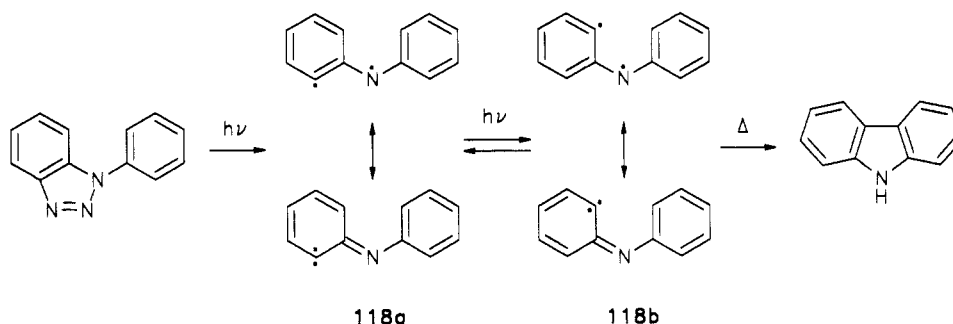
triplet diphenyl ketene for *s-E*, and ISC to the singlet carbene with subsequent Wolff rearrangement for *s-Z*. IR detection reveals that diphenyl ketene is the only major product in Ar matrices at 10 K.<sup>202</sup>

Irradiation ( $\lambda > 300$  nm) of 4,5-diphenyl-1,2,3-thiadiazole powder at 77 K produced thioketocarbene 112, which was identified by its triplet ESR spectrum (Table IX).<sup>203</sup> Again, the conformation of 112 is controlled by the conformation of the precursor, and consequently only the *s-E* rotamer was observed. Above 77 K 112 decays with first-order kinetics and from the Arrhenius plot values of  $E_a = 5.4$  kcal/mol and  $\log A = 9.1$  were determined. After warming to room temperature, diphenyl thioketene was formed with a characteristic violet color.<sup>203</sup>

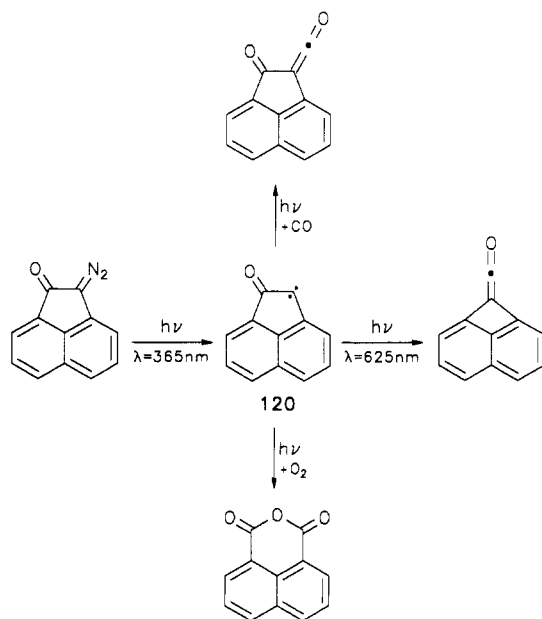
Dibenzoylcarbene (113) was produced by 77 K photolysis ( $\lambda > 335$  nm) of dibenzoyldiazomethane powder.<sup>204</sup> Three conformers are possible: *s-E,s-E*; *s-Z,s-Z*; and *s-E,s-Z*. On the basis of ESR data, the *s-E,s-Z* conformer was identified as the major rotamer while the *s-E,s-E* conformer is a minor constituent. In a glass matrix only the major conformer was observed.<sup>204</sup> The relatively low *D* value observed for 113 (Table IX) has given rise to question the assignment of the ESR spectrum.<sup>39</sup>

While acyclic ketocarbenes can frequently be observed by ESR spectroscopy, additional electronic or steric stabilization of the carbenes relative to the ketenes is required to obtain concentrations high enough for IR detection. Wolff rearrangement of 6-oxo-2,4-cyclohexadienylidene (115) is very rapid, and irradiation ( $\lambda > 350$  nm) of 6-diazo-2,4-cyclohexadienone in Ar at 15 K produced only cyclopentadienylidene ketene.<sup>205</sup> Substitution of oxygen by N-R (R = H, CH<sub>3</sub>, Ph) gives iminocyclohexadienylidenes 116–119. Carbenes 116–119 were generated by irradiation of the corresponding benzotriazoles as powder at 77 K and characterized by their triplet ESR spectra.<sup>206</sup> Two rotamers 118a and 118b were observed, which rapidly interconvert on irradiation, but not thermally at temperatures up to 130 K (Scheme VI). 118b is thermally less stable than

## Scheme VI



## Scheme VII



118a and decays with first-order kinetics presumably to give carbazole (the sole product of solution-phase photolysis). In the range 104–124 K the activation parameters were determined to be  $E_a = 5.2 \pm 0.5$  kcal/mol and  $\log A = 6.5 \pm 0.8$ . The low  $\log A$  value indicates that ISC to the singlet carbene is rate determining and  $E_a$  corresponds to  $\Delta E_{ST}$ .

The first IR spectroscopic detection of a  $\sigma$ -ketocarbene was reported by Chapman et al.<sup>207,208</sup> Acenaphthylenylidene (120) was generated by irradiation ( $\lambda = 365 \pm 8$  nm) of 2-diazo-1(2H)-acenaphthylenone, matrix isolated in Ar at 15 K, and characterized by ESR (Table IX), UV-vis ( $\lambda_{\max} = 621.3, 597.1, 590.3, 573.4, 563.2$  nm), and IR (1665, 1015, 767  $\text{cm}^{-1}$ ) spectroscopy.<sup>208</sup> Irradiation at longer wavelength ( $\lambda = 625 \pm 8$  nm) produces the ketene. Carbene 120 was trapped in oxygen-doped Ar matrices (20%  $\text{O}_2$ ) to give 1,8-naphthalic anhydride, and in carbon monoxide-doped matrices (0.25%) to give the ketoketene (Scheme VII).

Ketocarbenes 121 and 122 were produced and characterized similarly (Table IX).<sup>208</sup> The  $\text{C}=\text{O}$  stretching modes  $\nu_{\text{C}=\text{O}}$  of 121 and 122 are observed at 1658 and 1679  $\text{cm}^{-1}$ , and the longest wavelength visible absorptions at 643 and 663 nm, respectively. In contrast to 120 and 121, where on irradiation of the diazo precursor always a large fraction of ketene was formed, carbene 122 was produced in a very clean reaction. The Wolff rearrangement was suppressed completely, and the ketene formed only on prolonged long wavelength

irradiation. These experiments reveal that ketocarbenes 120–122 are the primary photoproducts of the corresponding diazo ketones, and the Wolff rearrangement is induced photochemically by irradiation into long wavelength triplet-triplet absorptions of the carbenes. It was also concluded that the Wolff rearrangement is not inhibited by the ring strain of the ketenes, but rather by stereoelectronic factors in the carbenes.<sup>208</sup>

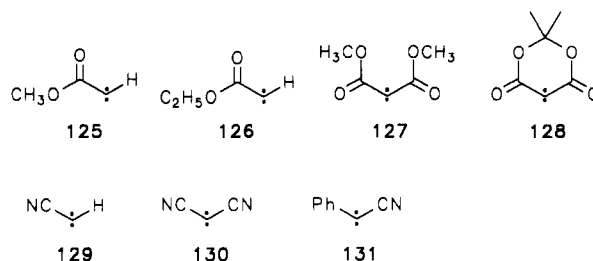
Tomioka et al. investigated the matrix photochemistry of 1,3-bis(diazo)indan-2-one.<sup>209,210</sup> The two molecules of nitrogen were split off stepwise, and ketocarbene 123 was identified by ESR (in a MTHF glass at 18 K, Table IX), IR (Ar, 8 K,  $\nu_{\text{C}=\text{O}}$  1647  $\text{cm}^{-1}$ ), and chemically by trapping with oxygen. The thermal oxygenation of 123 in 1%  $\text{O}_2$ -doped Ar matrices at 35 K resulted in the formation of a carbonyl O-oxide, which was identified by its intense O–O stretching vibration at 970 and 945  $\text{cm}^{-1}$ .<sup>209</sup>

A five-membered heterocyclic carbene is 2,3-dihydro-2-oxo-1-methyl-indol-3-ylidene (124), which was generated by irradiation of the corresponding diazo precursor and characterized by ESR spectroscopy.<sup>211</sup> In solution the carbene dimerizes to give isoindigo.

## 2. Carboxy and Nitrile Groups at the Carbene C-Atom

Carbalkoxycarbenes are of interest for the synthesis of functionalized cyclopropanes.<sup>212</sup> The ESR spectra of carbomethoxycarbene (125) and carbethoxycarbene (126) (Chart IX), generated by irradiation of the diazo precursors in a variety of frozen solutions or vacuum-deposited matrices, were reported by Hutton and Roth (Tables X).<sup>213</sup> Matrices containing benzophenone or acetophenone gave a higher signal intensity than other matrices, which indicates that photosensitization takes place. In the temperature range 10–40 K the Curie law was obeyed, indicating a triplet ground state for 125 and 126, while at higher temperatures the signals disappeared irreversibly. Geometric isomerism was

### Chart IX





**Table X. ESR Data of Carbalkoxy- and Cyanocarbenes (Chart IX)**

carbene	matrix <sup>a</sup>	T, K	$D/hc$ , cm <sup>-1</sup>	$E/hc$ , cm <sup>-1</sup>	$E/D$	comments	ref
125	MCH	10	0.617	0.053	0.0859	<i>s-E</i>	213
			0.663	0.030	0.0452	<i>s-Z</i>	
126	MCH	10	0.616	0.053	0.0860	<i>s-E</i>	213
			0.661	0.031	0.0469	<i>s-Z</i>	
127	MTHF	<i>b</i>	0.604	0.031	0.0513		39
			0.606	0.051	0.0842		
			0.615	0.034	0.0553		
128	MTHF	<i>b</i>	0.578	0.035	0.0606		39
129	PCTFE	77	0.8629	0	0.0		177
130	fluorol	4	1.002	<0.002	<0.002	linear	220
	HFB	4		0.0033		bent	220
131	<i>b</i>	<i>b</i>	0.6478	0.0033	0.0219		144

<sup>a</sup> See Table I. <sup>b</sup> Not specified.

observed for both carbenes, with the *s-E* rotamers being formed in higher yields than the *s-Z* isomers. An interconversion of the isomers was not observed.<sup>39,213</sup>

Three different ESR spectra of dicarbomethoxycarbene (127) were observed after irradiation of dimethyl diazomalonate in an MTHF glass.<sup>39</sup> By comparison with the cyclic derivative 128, which has a smaller  $D$  value than any of the  $D$  values determined for 127 (Table X), evidence was given that only two rotamers in different matrix sites were present in the matrix.

The ESR spectrum of cyanocarbene 129 reveals the similarity of the  $\pi$ -system with that of propargylene. In poly(chlorotrifluoroethylene) at 77 K the  $E$  parameter is zero, which indicates a linear structure.<sup>177</sup> A low  $E$  value could also be caused by motion of the H-atom in the matrix, as it has been observed for CH<sub>2</sub>, and thus without hyperfine data the assignment of the structure is not definitive.<sup>46,214</sup> The UV-vis and IR spectrum of 129 and several of its isotopomers (DCCN, HC<sup>13</sup>CN, HCC<sup>15</sup>N), matrix isolated in Ar at 12 K, was reported by Dendramis and Leroy.<sup>215</sup> The normal coordinate analysis provides evidence for the linear, allenic structure, which was also deduced from the gas-phase microwave spectrum.<sup>216</sup> In the microwave study it was stated that an HCC angle as small as 138° would have been detected, even if the potential surface for the H-C-C bent is flat. *Ab initio* calculations both on RHF or UHF levels predict a bent triplet ground state,<sup>217,218</sup> while inclusion of CI leads to a linear structure.<sup>219</sup> Schaefer et al. concluded from *ab initio* calculations including correlation effects that 129 is a quasilinear molecule with an H-C-C angle of ~138° and a barrier to linearity of about 2 kcal/mol.<sup>214</sup> Thus there is still a discrepancy between theory and experiment.

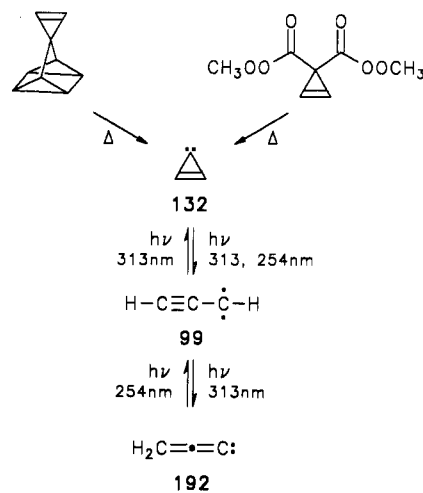
Dicyanocarbene (130) was generated in low-temperature matrices by UV irradiation of dicyanodiazomethane and characterized by ESR<sup>220</sup> and IR<sup>221</sup> spectroscopy. The ESR spectra in organic glasses reveal the extensive delocalization of both unpaired electrons.<sup>220</sup> The  $E$  value depends on the solvent and is <0.002 cm<sup>-1</sup> in fluorolube but 0.0033 cm<sup>-1</sup> in hexafluorobenzene, indicating a linear structure in the former and a slightly bent (not more than 10–15°) structure in the latter solvent. A vibrational analysis of the IR spectrum obtained in Ar at 10 K is consistent with a linear structure.<sup>221</sup> Again—in contrast to the experiment—theory predicts a bent structure with a C-C-C angle of 133° and a barrier to linearity of 9 kcal/mol.<sup>222</sup>

ESR data of cyanophenylcarbene (131) were reported.<sup>77</sup> The  $E$  value is similar to other arylcarbenes, and thus a bent structure can be deduced (Table X).

## C. Cyclic Carbenes

### 1. Cyclopropenylidene

Recent *ab initio* calculations of C<sub>3</sub>H<sub>2</sub> species predict that singlet cyclopropenylidene 132 is the global minimum of the C<sub>3</sub>H<sub>2</sub> hypersurface.<sup>224a</sup> Maier et al. generated 132 by FVP of a quadricyclane derivative<sup>225</sup> or a perester<sup>181</sup> and subsequent trapping of the pyrolysis products in Ar at 10 K (Scheme VIII). Carbene 132

**Scheme VIII**

was identified by its IR spectrum and shows absorptions at 1279, 1063, 888, and 789 cm<sup>-1</sup>, in excellent agreement with the calculated vibrational modes.<sup>224,225</sup> Additional evidence comes from the observed photochemical interconversion with propargylene 99 and vinylidene-carbene 192 (Scheme VIII, see also section III.D.2). No ESR signal was observed, which indicates a singlet ground state—again in accordance with theory. Preparative scale pyrolysis of the quadricyclane derivative produced benzene almost quantitatively, and in the presence of water the products of O-H insertion, cyclopropenol and dicyclopropenyl ether, were isolated.<sup>225</sup> After spectroscopic characterization in the laboratory, Thaddeus et al. were able to show that 132 is one of the most abundant molecules in interstellar molecular clouds.<sup>226</sup>

### 2. Cyclopentadienylidene, Indenylidene, and Fluorenylidene

Cyclopentadienylidene (133, Chart X) was one of the first carbenes to be examined by matrix isolation spectroscopy. An attempt to isolate 133 in a N<sub>2</sub> matrix was reported as early as 1959 by DeMore, Pritchard, and Davidson,<sup>2</sup> but the authors were only able to observe the dimer fulvalene. ESR data of 133 were published in 1964 by Wasserman et al.<sup>227</sup> The ZFS parameters [ $|D/hc| = 0.4089$  and  $|E/hc| = 0.0120$  cm<sup>-1</sup>] point to a structure with C<sub>2v</sub> symmetry, with one unpaired electron localized at the carbene center, while the other electron is delocalized over the five-membered ring (Table XI). Fifteen years later Baird, Dunkin, and Poliakoff reported IR and UV spectra of 133,<sup>29</sup> and a full-paper,

Chart X

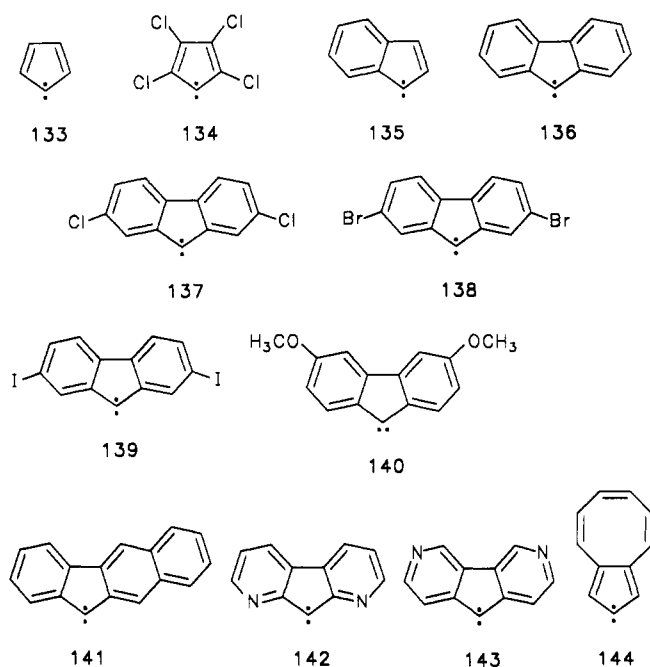


Table XI. ESR Data of Cyclopentadienylidene, Indenylidene, and Fluorenylidene Derivatives (Chart X)

carbene	matrix <sup>a</sup>	T, K	$D/hc$ , cm <sup>-1</sup>	$E/hc$ , cm <sup>-1</sup>	$E/D$	ref
133	HFB, HCB	4,77	0.4089	0.0120	0.0293	227
135	HFB, HCB	4,77	0.3777	0.0160	0.0424	227
136	FL <sup>b</sup>	77	0.4078	0.0283	0.0694	69
	DAF <sup>c</sup>	77	0.40923	0.02828	0.0691	95
137	MTHF	8	0.4158	0.0287	0.0690	242
138	neat	77	0.3991	0.0279	0.0699	243
	MTHF	8	0.4134	0.0281	0.0680	242
139	MTHF	8	0.4088	0.0277	0.0678	242
141	MTHF	3.8	0.39	0.030	0.077	245
142	MTHF	4	0.442	0.029	0.0656	246
143	MTHF	4	0.438	0.0306	0.0699	247
144	MTHF	17	0.2401	0.0044	0.0183	249

<sup>a</sup> See Table I. <sup>b</sup> Fluorenone. <sup>c</sup> Diazofluorene single crystal.

including spectroscopy with linearly polarized light, appeared in 1981.<sup>228</sup> The IR spectrum is relatively simple and does not exhibit particularly characteristic features (a band at 703 cm<sup>-1</sup> was assigned to a C-H out-of-plane deformation mode). In the UV a broad absorption with  $\lambda_{\max}$  at 296 nm was detected. Further matrix work on 133 dealt with its reactions with triplet oxygen<sup>229-232</sup> and with ethylene.<sup>233</sup> Tetrachlorocyclopentadienylidene (134) was a target of Dunkin's group in Glasgow.<sup>234</sup> Compared with 133, the long wavelength absorption is red-shifted in 134 by ca. 40 nm and exhibits a distinct vibrational fine structure with spacings of approximately 1100 cm<sup>-1</sup>. This vibration in the excited state is nicely reflected in the ground state with a prominent IR absorption at 1127 cm<sup>-1</sup>. In the same paper, Bell and Dunkin also describe the spectroscopic properties of indenylidene (135).<sup>234</sup> Benzoannulation in 135 shifts the long wavelength UV absorption further to the red: the molecule exhibits a very weak band system between 400 and 440 nm with a sharp  $\lambda_{\max}$  at 440 nm. The ESR spectrum, however, is less affected by the additional benzene ring; with  $D = 0.3777$  and  $E = 0.0160$  cm<sup>-1</sup> the  $\pi$ -spin is only slightly better delo-

calized than in 133.<sup>227</sup> Further matrix studies on 134 and 135 emphasized their reactions with <sup>3</sup>O<sub>2</sub>.<sup>232,235,236</sup>

Like many other triplet carbenes, fluorenylidene 136 was first examined by ESR spectroscopy. Values for the ZFS parameters were published by Trozzolo et al. in 1962 ( $|D/hc| = 0.407$   $|E/hc| = 0.027$  cm<sup>-1</sup>),<sup>68</sup> soon after, a measurement of <sup>13</sup>C-hyperfine splitting was reported (Table XI).<sup>69</sup> The ZFS parameters are similar to those of diphenylcarbene; if  $E/D$  is taken as a crude measure for the amount of s character at the carbene center, the angle at the divalent carbon atom would have to range around 150°, which is not possible if one presupposes that the geometry of fluorenylidene must be similar to that of fluorene. Wasserman et al. therefore suggested "bent bonds" at the carbene center. A series of papers on ESR spectroscopy applied to 136 were to follow these early publications: Brandon et al.<sup>95</sup> (measurement in diazofluorene single crystal, including <sup>13</sup>C-hyperfine splitting), Barash et al.<sup>67b</sup> (generation of 136 from 9,9-diazidofluorene), Moser et al.<sup>67a</sup> (use of the sodium salt of fluorenone tosylhydrazone as photolytical carbene precursor). Electron nuclear double resonance (ENDOR) measurements on 136, which were performed by Hutchison and Pearson,<sup>237,238</sup> yielded values for the spin densities in the molecule: positive spin density is found at the carbene center, at the bridgehead carbon atoms, and on C-1 and C-3.

The optical absorption spectrum of fluorenylidene, although subject of some controversy in recent years, seems to be established. In the visible range, the spectrum consists of two bands at 470 (strong) and 440 nm.<sup>239</sup> In order to obtain the spectrum, the measurements had to be performed at 10 K, as 136 reacts with the solvent used (MTHF) within seconds at 77 K. The matrix spectrum is consistent with the spectrum obtained by laser-flash photolysis (LFP) in acetonitrile at room temperature.<sup>239</sup> An absorption at 400 and 497 nm, which earlier studies<sup>240,241</sup> had assigned to triplet 136, could be reassigned to a nitrile ylide and the 9-fluorenyl radical, respectively. At the same time, the early assignment of the 470-nm transition to singlet 136 had to be revised (the singlet excited state of 136 proved to be invisible in the LFP studies). Measurements in Ar matrix, performed by Bell and Dunkin<sup>234</sup> and by Hess,<sup>123</sup> resulted in the observation of UV bands at 462, 453, 436, and 251 nm (462 nm being the strongest one in the visible range), which is also consistent with the results obtained by Grasse et al.<sup>239</sup> in MTHF glass and in acetonitrile at room temperature, and by Closs et al.<sup>114</sup> (The latter only noted a similarity in the spectra of diphenylcarbene 17 and 136, but did not give any more detailed information.)

Along with UV data in Ar matrix, Bell and Dunkin also published the infrared spectrum of 136 (absorptions at 1559, 1035, 772, 762, 755, 743, 729, and 713 cm<sup>-1</sup>).<sup>234</sup> Somewhat different values were reported by Hess,<sup>123</sup> who observed bands at 1630 (s), 1418, 1215, 1025, 760 (vs), 750, 720 (vs) cm<sup>-1</sup>.

A series of 2,7-dihalofluorenylidenes were the subject of work done by Schuster's group<sup>242</sup> and of an earlier paper by Murahashi et al.<sup>243</sup> The study by Rak et al.<sup>242</sup> was designed mainly to elucidate the question of how ground-state triplet carbenes manage to react very rapidly with typical singlet-carbene quenchers such as methanol. It failed to provide a definitive answer to

this problem, but among other interesting results, it yielded valuable spectroscopic information on 2,7-dichloro-, 2,7-dibromo-, and 2,7-diiodofluorenylidene (137, 138, and 139, respectively). From the ESR spectra no internal heavy-atom effect could be discerned, as the ZFS parameters of the halogenated derivatives are very close to that of parent fluorenylidene. Additionally, iodine substitution has no observable influence on the  $g$  values. (Significant spin-orbit coupling due to the heavy-atom effect would be expected in this case, if anywhere.) More significant substituent effects were observed in 3,6-dimethoxyfluorenylidene (140),<sup>244</sup> which, unlike almost all aryl carbenes discussed thus far, has a singlet ground state. This fact was revealed by the lack of an ESR signal in combination with completely stereospecific cycloaddition and rate constants of its reaction with methanol close to the diffusion-controlled limit. Its optical absorption spectrum in MTHF glass at 77 K is blue-shifted with respect to parent 136 ( $\lambda_{\max}$  = 409 and 429 nm); at the same time, extinction coefficients are smaller. Another carbene with predominantly singlet chemistry in solution is 2,3-benzofluorenylidene (141).<sup>245</sup> ESR measurements in MTHF glass showed that 141 has a triplet ground state, while the combination of kinetics (laser-flash photolysis) with product studies revealed that  $\Delta G_{ST}$  ( $\Delta G_S - \Delta G_T$ , a positive value meaning that the triplet state is lower in energy than the singlet) must be very small. (Schuster et al. reported a value of ca. 1 kcal/mol.) The optical absorption spectrum of 141 (MTHF glass, 77 K) is characterized by three bands at 485, 459, and 434 nm; it is therefore similar to that of 136.

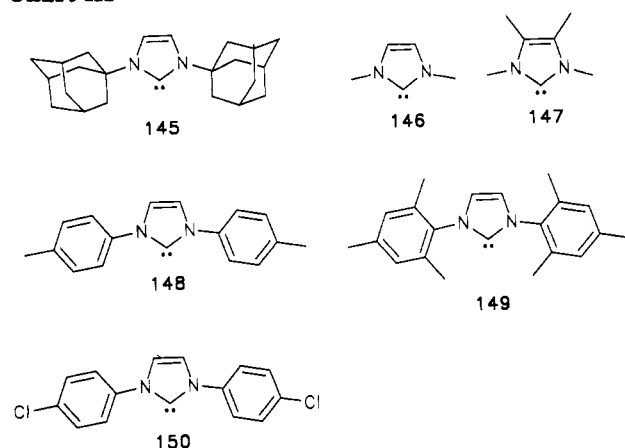
The triplet ground states of 1,8- and 3,6-diazafluorenylidene (142 and 143, respectively)<sup>246-248</sup> also exhibit only slightly different properties, if compared to triplet 136. What makes these carbenes interesting, and in some way unique, is the unusual reactivity of their singlet excited states. So does singlet 142 react with cyclohexane at the diffusion-controlled limit, and it does not discriminate between benzene and methylstyrene. This kind of reactivity so far was only known from  $^1\text{CH}_2$ ! In order to explain their observations, Li and Schuster therefore suggested a high proportion of  $\pi^2$ -character at the carbene centers in both singlet carbenes, induced by through-space and/or through-bond electronic interaction with the nitrogen atoms.

A carbene with an unusual electronic structure is bicyclo[6.3.0]undeca-2,4,6,8,11-pentaen-10-ylidene (144).<sup>249</sup> From the ESR spectrum in MTHF at 17 K a  $D$  value of  $0.2401\text{ cm}^{-1}$  was obtained, which implies a large contribution of biradical character to the electronic structure of 144 (Table XI). In Ar at 12 K IR absorptions at 800 and  $687\text{ cm}^{-1}$  and UV-vis absorptions with maxima at 546 and 506 nm were assigned to the carbene.  $\text{O}_2$  trapping produced a carbonyl oxide with the  $\pi-\pi^*$  transition red-shifted to 582 nm.

### 3. Imidazol-2-ylidenes

In 1962 Wanzlick was able to demonstrate that imidazolidin-2-ylidenes form a class of relatively stable nucleophilic carbenes.<sup>250</sup> His prediction that  $\pi$ -interaction leading to carbanionic centers would further stabilize the carbenes was recently confirmed by the isolation of stable imidazol-2-ylidenes. Arduengo et

Chart XI



al. was able to synthesize several derivatives of these singlet carbenes (145–150, Chart XI), which are completely stable even at room temperature.<sup>251,252</sup> Although matrix isolation is not necessary for the spectroscopic characterization of these imidazol-2-ylidenes, they will be treated here because of their relation to cyclopentadienyliidene (133) and for sake of completeness.

The first imidazol-2-ylidene characterized was the 1,3-diadamantyl derivative 145, synthesized by deprotonation of 1,3-di-1-adamantylimidazolium chloride.<sup>250</sup> The deprotonation of imidazolium chlorides proved to be a general method for the synthesis of imidazolylidenes.<sup>251</sup> Carbene 145 forms colorless crystals with a melting point of  $240^\circ\text{C}$  and is easily characterized by spectroscopic methods including X-ray diffraction.<sup>250</sup> While for 145 both electronic effects<sup>253</sup> and steric hindrance might contribute to the stability, the isolation of sterically unencumbered carbenes, such as 146 or 147, demonstrates that steric factors are unimportant for the stabilization.<sup>251</sup> The stabilization is mainly due to a combination of the electron-donating properties of the electron-rich  $\pi$ -system and the  $\sigma$ -electron-withdrawal effect of the electronegative N atoms adjacent to the carbene center, which in turn leads to an increase of the singlet-triplet gap.<sup>253</sup> From X-ray diffraction studies N–C–N bond angles between  $101.2^\circ$  (148) and  $102.2^\circ$  (145) were determined, which are significantly smaller than those of the corresponding imidazolium salts. The chemistry of imidazol-2-ylidenes, although not yet studied in great detail, is also remarkable. Thus carbene 145 forms a stable ylide with iodopentafluorobenzene.<sup>254</sup> A thorough investigation of the chemistry of these carbenes will have a large impact on the understanding of the properties of singlet carbenes.

### 4. Cyclohexadienyliidenes

*a. 2,5-Cyclohexadienyliidenes.* 4-Substituted 2,5-cyclohexadienyliidenes are the only cyclohexyliidenes for which spectroscopic data are reported in literature. Because of very rapid 1,2-H shifts, cyclic carbenes with aliphatic  $\alpha$ -hydrogen atoms are not stable even under the condition of matrix isolation. 2,5-Cyclohexadienyliidene (151, Chart XII) is a benzene isomer for which experimental evidence has not been presented, so far. Jones et al. investigated the solution and gas-phase chemistry of 4,4-dimethylcyclohexadienyliidene (152)<sup>255</sup> and 4,4-dimethyl-4-silacyclohexadienyliidene (153),<sup>256</sup> but again spectroscopic data have not been reported

Chart XII

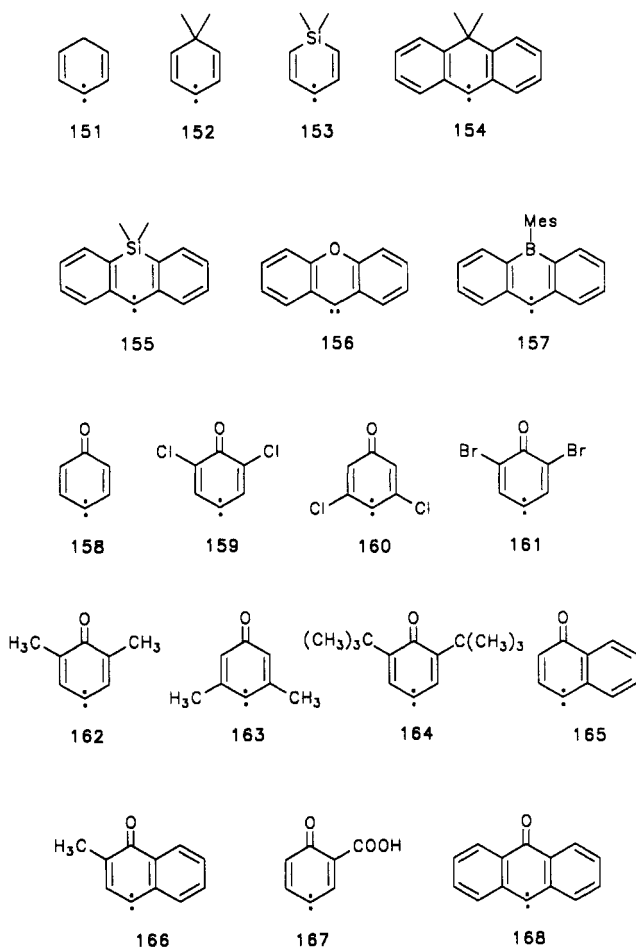


Table XII. ESR Data of 4-Oxo-2,5-cyclohexadienylidenes (Chart XII)

carbene	matrix <sup>a</sup>	T, K	D/hc, cm <sup>-1</sup>	E/hc, cm <sup>-1</sup>	E/D	ref
155 <sup>b</sup>	EPA	40	0.391	0.0215	0.055	258
157	MTHF	4.6	0.360	0.0156	0.043	262
158	DCB	4,77	0.3179	0.0055	0.017	263
159	neat	4,77	0.3284	0.0086	0.026	263
160	TCB	4,77	0.3470	0.0010	0.0029	263
164	neat	93	0.3141	0.0051	0.016	299
165	neat	4,77	0.3333	0.0112	0.034	263
168 <sup>c</sup>	BZP	77	0.365	0.0177	0.048	265
	neat	77	0.3638	0.0176	0.048	32

<sup>a</sup> See Table I. <sup>b</sup> Linear Curie-Weiss plot. <sup>c</sup> Stable at 77 K, signals disappear slowly at 160 K.

for these carbenes. From a LFP study Admasu and Platz concluded that in 10,10-dimethyl-9-anthrylidene (154) the singlet and triplet states are essentially degenerate.<sup>257</sup> ESR (Table XII)<sup>258</sup> as well as electronic absorption spectra ( $\lambda_{\max} = 312, 345, \text{ and } 510 \text{ nm}$ )<sup>259</sup> of 10,10-dimethyl-10-sila-9-anthrylidene (155) were reported by Iwamura et al. The triplet ground state of 155 was clearly established by the observation of a triplet ESR signal and a linear Curie-Weiss plot<sup>258</sup> and is consistent with the rapid reaction with  $^3\text{O}_2$  to form a carbonyl oxide in solution at room temperature.<sup>260</sup> The relatively large  $E$  value indicates a decrease of the bond angle at the carbene center.<sup>258</sup>

Two further hetero-substituted cyclohexadienylidenes were investigated in frozen media by Schuster et al.: 9-xanthylidene (156)<sup>261</sup> and 9-mesityl-9,10-dihydro-9-boraanthrylidene (157).<sup>262</sup> Irradiation of 9-diazoxan-

thene in methylcyclohexane at 77 K produced a species with UV absorptions at 393, 385, and 376 nm, which were assigned to 156.<sup>261</sup> No ESR signal was observed, and from the chemical reactivity (stereospecific addition to styrenes, rapid insertion into O-H bonds and no reaction with hydrocarbons) observed in LFP and trapping experiments a singlet ground state with  $\Delta G_{\text{ST}} < -4 \text{ kcal/mol}$  was deduced.

In contrast to 156, triplet ESR signals, which were stable for several hours at 77 K, could readily be obtained for 157 in MTHF (Table XII). The zero-field parameters indicate that 157 is a nonlinear triplet carbene with a large one-center interaction.<sup>262</sup> In the UV-vis a sharp, intense band at 359 nm and broader absorptions at 460 and 530 nm are assigned to the carbene. On the basis of LFP and trapping experiments it was concluded that  $\Delta G_{\text{ST}}$  in boraanthrylidene 157 is considerably larger than in fluorenylidene 136. This is mainly a consequence of the larger bond angle at the carbene center in 157.

*b. 4-Oxo-2,5-cyclohexadienylidenes.* In contrast to 2-oxo-3,5-cyclohexadienylidene (115), which rapidly undergoes Wolff rearrangement and therefore is not accessible to matrix isolation spectroscopy (see section III.B), 4-oxo-2,6-cyclohexadienylidene (158) and several of its derivatives were characterized by ESR, UV-vis, and IR spectroscopy.

In 1964 Wasserman and Murray<sup>263</sup> reported the first ESR spectra of carbene 158 and several derivatives (Table XII). UV irradiation of powdered samples of the corresponding quinone diazides (either neat or as solid solution in *p*-dichlorobenzene) at 77 or 4 K produced carbenes 158–160 and 165 in their triplet ground states. The parent carbene 158 has a comparatively small  $D$  value of  $0.3179 \text{ cm}^{-1}$ , which indicates a large average distance of the unpaired electrons. One of the unpaired electrons is mainly localized in the  $\sigma$ -plane at carbene center C-1, as in the phenyl radical, while the other is delocalized in the  $\pi$ -system, as in the phenoxyl radical. The  $\pi$ -spin density at C-1 was estimated to approximately 0.4, similar to the para position of a phenoxy radical. The  $D$  values of the substituted carbenes are somewhat larger (Table XII). The small values of  $E$  ( $0.0010$ – $0.0112 \text{ cm}^{-1}$ ) were rationalized by assuming “bent bonds” at C-1.<sup>263</sup> The ESR spectrum of a matrix-isolated sample of 158 is similar to that of the powder sample; between 23 and 45 K the Curie law is obeyed which proves the triplet ground state.<sup>264</sup>

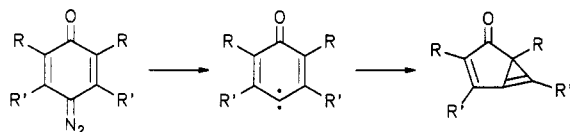
Anthrynylidene 168 was generated by photolysis of 9-diazo-10-anthrone in various organic glasses and characterized by ESR (Table XII)<sup>32,265–268</sup> and UV-vis<sup>267,268</sup> spectroscopy. In MTHF at 4 K a strong sharp UV band at 352 nm and two weak broad bands at 523 and 564 nm were found. The conclusion of these studies (including LFP experiments) was that 168 is a ground state triplet carbene with  $\Delta G_{\text{ST}}$  of  $5.8 \text{ kcal/mol}$ .<sup>268</sup> Murai et al. reported the formation of quintet state radical pairs if the neat diazo precursor was photolyzed at low temperature.<sup>32</sup>

IR and UV spectra of matrix-isolated oxocyclohexadienylidenes 158, 159, and 161–167 have been reported by our group.<sup>264,269</sup> In the UV-vis spectra broad absorptions exhibiting vibrational fine structure around 500–600 nm and sharp absorptions at 370–380 nm are

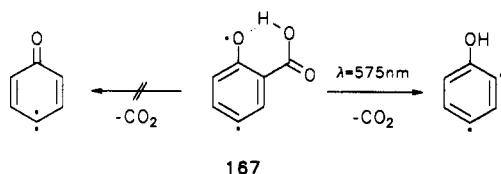
characteristic of these carbenes.<sup>270</sup> The former band system is rather sensitive while the sharp absorptions are insensitive to substitution. A very sharp absorption at 395 nm was also reported for the phenoxyl radical,<sup>271</sup> which reveals the similarity of the  $\pi$ -systems of this radical and the carbenes. In the IR the most characteristic absorptions are the C=O stretching vibrations in the range 1498–1558  $\text{cm}^{-1}$ , which indicates a C=O bond order of significantly less than 2,<sup>270</sup> and again demonstrates the delocalization of the  $\pi$ -system.

Chemical evidence for the oxocyclohexadienylidenes was also given. In oxygen-doped matrices the thermal formation of carbonyl *O*-oxides was observed for all carbenes,<sup>272,273</sup> and for 158, the carbonylation reaction in CO-doped matrices produced a ketene.<sup>264,269</sup>

The photochemistry of the carbenes—especially the vinylcarbene–cyclopropene rearrangement—was studied in some detail.<sup>269,270</sup> Only 162 proved to be quite stable on visible-light irradiation, while 158, 159, 161, 163, 165, and 166 rearranged to strained 1,3-bridged cyclopropenes in yields that were highly dependent on substituents. The cyclopropenes are thermally highly labile, metastable compounds and even in Ar at 10 K they rearrange back to the carbenes quantitatively. The half-life depends on substituents, matrix, and temperature and is in the order of several weeks for the most stable benzoannulated carbenes 165 and 166 in Ar at 10 K. Irradiation with visible or infrared light also produced the carbenes quantitatively, while UV irradiation gave ketenes and other products irreversibly.



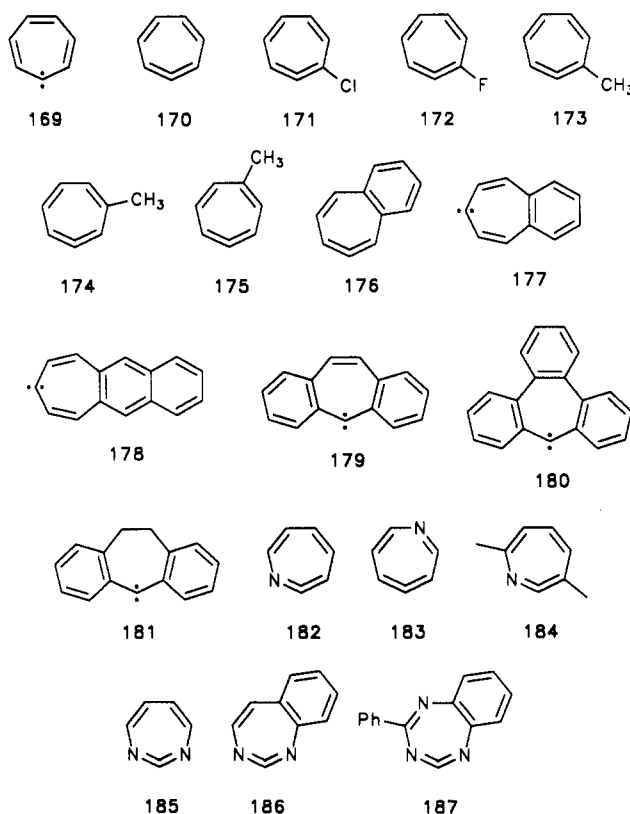
Carbene 167 readily decarboxylates on irradiation with red light ( $\lambda > 630$  nm) to give *m*-dehydrophenol, while the vinylcarbene–cyclopropene rearrangement is of minor importance, only.<sup>274</sup>



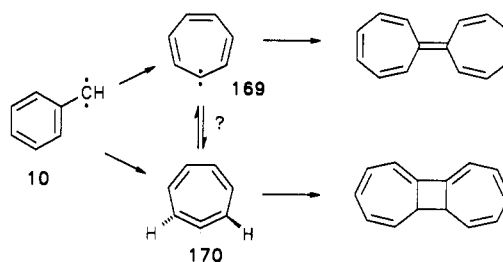
### 5. Cycloheptanylidenes

The  $\text{C}_7\text{H}_6$  hypersurface, and especially the carbene/cycloheptatrienylidene of phenylcarbene and cycloheptatrienylidene (169, Chart XIII), have attracted much attention during the past years. Several cycloheptatrienylidenes have been characterized spectroscopically in matrices, but still many details, e.g. the relation of 169 and cycloheptatetraene (170), are not yet clear. Three seven-membered ring species, which in principle can interconvert thermally or photochemically, must be considered: the planar ( $C_{2v}$  symmetry) triplet (ground state) carbene T-169, the planar ( $C_{2v}$  symmetry) singlet carbene S-169, and the nonplanar, chiral ( $C_2$  symmetry) allene 170 (Scheme IX). Depending on the level of calculation, S-169 is predicted to be a true minimum or a transition state between the two enantiomers of 170.<sup>275,276</sup> From *ab initio* calcula-

Chart XIII



Scheme IX



tions Janssen and Schaefer concluded that 170 lies approximately 16 kcal/mol below S-169,<sup>277</sup> which in turn is 4.5 kcal/mol more stable than T-169.<sup>277</sup> This is in obvious contradiction to the detection of T-169 via ESR spectroscopy (vide infra). An explanation of this is that the geometries of singlet and triplet 169 are quite different, and at the triplet equilibrium geometry the singlet lies 6.7 kcal/mol higher!

The ring expansion of phenylcarbene (10) to cycloheptatrienylidene (169) was first demonstrated by trapping heptafulvalene—the dimer of 169—in solution experiments (Scheme IX).<sup>278</sup> These experiments do not rule out the formation of allene 170 as the ring-expanded product, because the dimer of 170 could thermally rearrange to heptafulvalene. Carbene 169 and cycloheptatetraene (170) are closely related, and therefore both isomers are treated in this chapter.

The first direct spectroscopic characterization of 170 and several of its derivatives was presented by Chapman et al. in a series of papers (Table XIV).<sup>72,76,279–281</sup> Irradiation ( $\lambda > 416$  nm) of phenylcarbene, matrix isolated in Ar at 10 K, yielded 170 in a clean reaction.<sup>72,280</sup> 170 was also produced by pyrolysis of phenyldiazomethane under FVP conditions or by photolysis of a variety of other precursors (Scheme X).<sup>279,280</sup>

## Scheme X

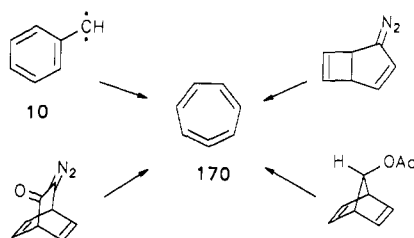


Table XIII. ESR Data of Cycloheptatrienylidene Derivatives (Chart XIII)

carbene	matrix <sup>a</sup>	T, K	$D/hc$ , $\text{cm}^{-1}$	$E/hc$ , $\text{cm}^{-1}$	$E/D$	ref
169	Ar	21	0.317	0.0087	0.0274	282
169	Ar	12	0.425	0.0222	0.0522	283
177	MCH, MTHF	4	0.52	0.021	0.0404	285
178	Ar	12	0.453	0.0193	0.0426	283
179	neat	77	0.3787	0.0162	0.0428	284
180	neat	77	0.4216	0.0195	0.0463	284
181	neat	77	0.3932	0.0170	0.0432	284

<sup>a</sup> See Table I.

The characterization of cycloheptatetraene 170 was based on spectroscopic and chemical evidence and on the results of isotopic labeling experiments.<sup>280</sup> The absence of a triplet ESR signal suggests a singlet ground state. In the IR weak absorptions at 1824 and 1816  $\text{cm}^{-1}$ , which after deuteration at C-1 were only slightly red-shifted, were assigned to the allene moiety (Table XIV). Another characteristic IR absorption frequently observed in cycloheptatetraenes is a medium intensity band at 1380  $\text{cm}^{-1}$ . The allene band was used to distinguish between 170 and bicyclo[4.1.0]heptatriene, another  $\text{C}_7\text{H}_8$  isomer which has to be considered as an intermediate in the phenylcarbene rearrangement. For the C=C stretching mode of a strained cyclopropene, such as the bicycloheptatriene, a lower frequency and a larger deuterium isotopic shift is expected. Compelling evidence for the formation of 170 rather than bicyclo[4.1.0]heptatriene came from elegant deuterium-labeling experiments.<sup>280</sup> The UV-vis spectrum of 170 is not characteristic, and above 300 nm no prominent absorption was detected. After evaporating the matrix and warming to room temperature, heptafulvalene was identified as the isolable dimer of 170.

In 1986 McMahon and Chapman<sup>282</sup> and Wentrup et al.<sup>283</sup> independently reported the first spectroscopic characterization of triplet cycloheptatrienylidene (169), generated by irradiation of matrix-isolated diazocycloheptatriene. The former group reported an intense triplet ESR signal with the ZFS parameters  $D = 0.317 \text{ cm}^{-1}$  and  $E = 0.0087 \text{ cm}^{-1}$ , indicating a planar or nearly planar structure of 169 (Table XIII).<sup>282</sup> Shorter wavelength irradiation irreversibly destroyed the signal. In the IR an absorption at 638  $\text{cm}^{-1}$  and several UV-vis bands in the range 530–220 nm were assigned to 169. It was also found that 169 neither thermally at temperatures up to 35 K, nor photochemically rearranges to 170.

Wentrup et al. reported different ZFS parameters for 169 ( $D = 0.425 \text{ cm}^{-1}$  and  $E = 0.0222 \text{ cm}^{-1}$ ),<sup>283</sup> and thus a different triplet species was observed and assigned to 169. The Curie law was not exactly obeyed, which could mean that on warming carbene 169 partially

Table XIV. IR Spectroscopic Data of Cycloheptatetraenes, Matrix Isolated in Ar at 10 K (Chart XIII)

carbene	C=C=C stretching, $\text{cm}^{-1}$	other, $\text{cm}^{-1}$	ref
170	1824w, 1816w	1380m	280
1-d-170	1822w, 1811w	1381m	280
4-d-170	1822w, 1815w		280
5-d-170	1820w, 1814w	1380m	280
171	1809m	1360w	280
172	1810m	1388m	280
3-d-172	1799m	1397s	280
173		1386m	281
$d_3\text{-CH}_3\text{-173}$	1819w, 1810w	1379m	281
174	1827vw, 1816w	1374m	281
175	1819w, 1811w	1379m	281
$d_3\text{-CH}_3\text{-175}$	1820w, 1810w	1366m	281
182	1895s	1348	290
183	1810		137
184	1899vw		294
185	1975s		295
186	2000s		295
187	2010s		296

rearranges to allene 170. Wentrup's results are in good agreement with reported data of benzoannulated cycloheptatrienylidenes (Table XIII), but so far the important question whether there is thermal equilibration between 169 and 170 is still open to discussion. Recently Blanch and Wentrup presented evidence that Chapman's carbene is a butylated species of unknown structure,<sup>283b</sup> and hopefully this discussion will be settled in near future.

Several derivatives of 170 were generated in low-temperature matrices and characterized spectroscopically. Irradiation of ortho-halogenated phenylcarbenes produced 1-halocycloheptatetraenes 171<sup>79,280</sup> and 172,<sup>280</sup> which exhibit a substantially enhanced intensity of the allene stretching mode (Table XIV). The rearrangements of the isomeric tolylcarbenes were studied in some detail.<sup>76,281</sup> Methylcycloheptatetraenes 174–175 are key intermediates in this interconversion and the proposed mechanism also explains the isomerization of benzocyclobutene to styrene.

In remarkable contrast to phenylcarbene (10), 1- and 2-naphthylcarbene (43 and 44, respectively) did not photochemically ring expand to benzocycloheptatetraenes, but rather cyclized to benzobicyclo[4.1.0]hepta-2,4,6-trienes.<sup>128</sup> Deuterium-labeling experiments suggest that the cyclopropenes are the primary products and are not formed by an expansion-cyclization mechanism. Consequently, the photochemical interconversion of carbenes 43 and 44 was not observed. FVP of either 1- or 2-naphthyl diazomethane produced mainly 1H-cyclobuta[de]naphthalene<sup>283c</sup> and small amounts of an unknown compound, which was tentatively assigned to 4,5-benzocycloheptatetraene (176).<sup>128a</sup>

Benzocycloheptatrienylidenes 177–180 were generated by irradiation of the corresponding diazocycloheptatrienes and characterized using ESR spectroscopy (Table XIII).<sup>283a,284,285</sup> On the basis of the ZFS parameters a triplet ground state with  $\Delta G_{\text{ST}}$  of 3.5–4 kcal/mol was estimated for 177. A transient UV-vis spectrum ( $\lambda_{\text{max}} = 380, 395 \text{ nm}$ ) of this carbene was presented by Horn et al.<sup>285</sup> The lack of evidence for the isomeric cycloheptatetraene under the same experimental conditions was rationalized by loss of aromatic resonance energy in the allene. A similar result—destabilization of the allene relative to the carbene—was found for the



naphthoannelated carbene 178<sup>283</sup> and is in accordance with solution studies of Hackenberger and Dürr<sup>286</sup> and Kirmse and Sluma.<sup>287</sup>

ESR spectra of carbenes 179 and 180 were reported by Moritani et al. in 1966 (Table XIII).<sup>284</sup> From the ZFS parameters it was concluded that 179 is planar, while 180 is substantially bent. For 179 a bond angle of 150° at the carbene center C-1 was estimated—close to the value obtained for diphenylcarbene 17—although the internuclear angle of the seven-membered ring is smaller. This result was interpreted in terms of “bent bonds” at C-1.

ESR<sup>284</sup> as well as UV-vis spectra ( $\lambda_{\text{max}} = 324, 348$  nm)<sup>113,288</sup> of dibenzocycloheptadienylidene (181) were reported, and by comparison with 17 the similarity of the  $\pi$ -systems of both carbenes became obvious. The close relation of 181 and 17—and the difference to fluorenylidene 136—is a consequence of the similar bond angle at the carbene center.<sup>288</sup> Platz et al. studied the kinetics of H-abstraction of 181 in polycrystalline toluene at 77 K by ESR spectroscopy and were able to observe the triplet radical pair as the principal first reaction product.<sup>289</sup> Nonexponential decay kinetics of this reaction was attributed to matrix site effects. In perdeuterated matrices only photochemical but no thermal D abstraction was observed, indicating a large kinetic deuterium isotope effect.

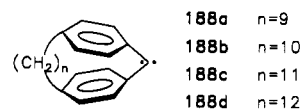
Azacycloheptatetraenes (or didehydroazepines) have a similarly long and complicated history as the cycloheptatetraenes. Phenyl azide as well as pyridyldiazomethanes provide convenient entries to the  $\text{C}_6\text{H}_5\text{N}$  hypersurface. Irradiation of matrix-isolated (Ar, 10 K) phenyl azide or 2-diazomethylpyridine produced 1-aza-1,2,4,6-cycloheptatetraene (182, Table XIV).<sup>290,291</sup> In the IR an intense absorption at 1895  $\text{cm}^{-1}$  was assigned to the  $\text{N}=\text{C}=\text{C}$  stretching mode (Table XIII). 3- and 4-diazomethylpyridine gave 1-aza-1,3,4,6-cycloheptatetraene (183) under similar conditions with the allene stretching mode at 1810  $\text{cm}^{-1}$ .<sup>137</sup> The photochemical interconversion of the isomeric triplet pyridylcarbenes and phenylnitrene (observed by ESR spectroscopy), as well as the interconversion of the singlet species 182 and 183 was explained in a common scheme with 182 as the primary product of the phenyl azide photochemistry.<sup>291</sup> In contrast to the photochemistry in Ar matrices, Platz et al. found triplet phenylnitrene being the major product in rigid glasses at 77 K and proposed that 182 is produced by secondary photolysis of the nitrene.<sup>292</sup> This was confirmed by Hayes and Sheridan, who were able to record the IR spectrum of phenylnitrene in Ar or  $\text{N}_2$  at 12 K. Photolysis of the nitrene finally produced 182.<sup>293</sup>

Other azacycloheptatetraenes characterized by IR spectroscopy are the dimethyl derivative 184, which was formed in very low yields only,<sup>294</sup> and a series of diazacycloheptatetraenes 185–187 with a strained carbodiimide group (Table XIV).<sup>283,295,296</sup>

## 6. Other Cycloalkylidenes

A group of diarylcarbenes building up on the [1.*n*]paracyclophane skeleton (188) were characterized by Staab, Maier, and co-workers.<sup>297</sup> The system, in which the carbene center was positioned in the methylene bridge, proved to be a good candidate for investigating the influence of the carbene C–C–C angle

on the ESR spectra as this parameter could be changed very conveniently by varying the length of the second bridge. A small para bridge also forces the rings to be parallel and practically perpendicular to the  $\pi$ -carbene orbital. Correspondingly, *D* values increase upon decreasing *n* from 12 to 9; the value of 0.4787 for 188a is one of the highest values ever reported for diarylcarbenes. It is consistent with previous findings that the triplet signals are more difficult to observe when *n* is decreased, which may be due either to a reduction in S–T splitting<sup>298</sup> or to a failure in detecting the corresponding carbene as the reactivity is enhanced.



## D. Unsaturated Carbenes

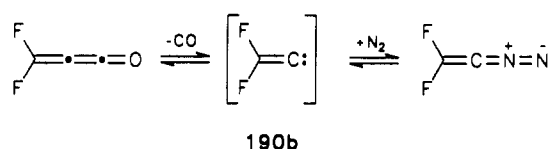
Vinylidenes and related unsaturated carbenes are highly reactive ground-state singlet carbenes of great value in preparative organic chemistry. Stang's 1978 review on unsaturated carbenes shows how broad the methods of generation and the range of reactions of these species is.<sup>300</sup> Nevertheless, due to the lack of appropriate photochemical precursors only a few direct experimental observations of vinylidenes and related carbenes have yet been reported. These include the infrared spectra and singlet–triplet gaps of vinylidene (189), fluorovinylidene (190a), and difluorovinylidene (190a), deduced from the photoelectron spectra of the corresponding vinylidene anions,<sup>301</sup> and the very remarkable matrix isolation studies of Maier et al. on the interconversion of  $\text{C}_3\text{H}_2$  isomers.<sup>180,181,225</sup>

### 1. Vinylidene

Singlet vinylidene (189) was calculated to be a shallow minimum on the  $\text{C}_2\text{H}_2$  potential energy surface.<sup>302–307</sup> The activation energy for the rearrangement to acetylene is very small, and one of the most recent values obtained by means of high level *ab initio* theory was as low as 0.9 kcal/mol.<sup>305</sup> A higher barrier was estimated for the excited triplet state of 189.<sup>302,308</sup> Several gas-phase studies on 189 have been published,<sup>309–311</sup> but because of the low barrier toward rearrangement matrix isolation has not been possible.

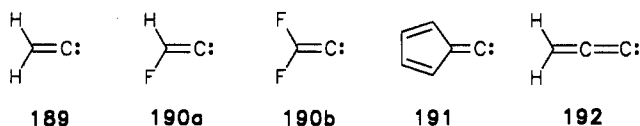
From the photoelectron spectrum of the fluorovinylidene anion the hydrogen isomerization barrier for 190a was estimated to  $2 \pm 1$  kcal/mol,<sup>301b</sup> in good agreement with theory.<sup>303</sup> For difluorovinylidene 190b, on the other hand, a much higher barrier was calculated,<sup>312–314</sup> and several experimental investigations concerning this molecule were published.<sup>301b,315,316</sup> Brahms and Dailey investigated the photochemistry of difluoropropadienone in Ar and  $\text{N}_2$  matrices.<sup>316</sup> Difluoropropadienone proved to be inert on short wavelength irradiation ( $\lambda > 185$  nm) in solid Ar, but in  $\text{N}_2$  matrix produced difluoroacetylene, CO, and small amounts of difluorodiazaoethene (Scheme XI). In a CO-labeled  $\text{N}_2$  matrix the carbonyl group of [1-<sup>13</sup>C]difluoropropadienone was exchanged on irradiation, however, no trace of 190b was detected in the IR spectra. According to *ab initio* calculations the reaction of 190b with CO as well as with  $\text{N}_2$  is strongly exothermic, which explains the difficulty of observing the carbene in the

## Scheme XI



presence of these molecules in the same matrix cage. Recently Lineberger et al. reported vibrational frequencies of singlet 190b at 1670, 905, and 510  $\text{cm}^{-1}$ , obtained from the photoelectron spectrum of the difluorovinylidene anion.<sup>301b</sup>

Cyclopentadienylidenecarbene (191) is an isomer of benzyne and was subject of experimental<sup>317</sup> semiempirical,<sup>318a</sup> and *ab initio*<sup>318b</sup> studies. The thermal interconversion of benzyne and 191 has been claimed,<sup>317b-d</sup> but so far no definitive experimental evidence for this rearrangement, nor any spectroscopic data of 191 have been presented.<sup>317a</sup> According to *ab initio* calculations 191 lies 31 kcal/mol above benzyne and is bound by less than 5 kcal/mol.<sup>318b</sup> Thus, matrix isolation of this carbene is a real challenge.



## 2. Vinylidenecarbene

Maier and co-workers were able to demonstrate that the three  $\text{C}_3\text{H}_2$  isomers cyclopropenylidene (132), propargylene (99), and vinylidenecarbene (192) interconvert photochemically in low-temperature matrices (Scheme VIII).<sup>180,181,225</sup>

Vinylidenecarbene (192) is the sole derivative of vinylidene isolated to date in a matrix and characterized by spectroscopic methods. The most intense absorptions of 192 were observed at 1952 and 1963  $\text{cm}^{-1}$  and assigned to the antisymmetric  $\text{C}=\text{C}=\text{C}$  stretching vibration. The assignment of IR data was supported by deuteration (both the mono- and dideuterio derivative were synthesized) as well as by calculations using high level *ab initio* methods (MP2/6-31G(d,p)).<sup>182,224a,319</sup> Irradiation of matrix-isolated cyclopropenylidene (132) with 313-nm light rapidly produced propargylene 99, which on further irradiation (20 h) gave vinylidenecarbene (192) in almost quantitative yield. At 254 nm, the isomerization was reversed to give 99, which again could be converted to 192 and small amounts of 132.

3. Carbon Oxides  $\text{C}_n\text{O}$  and Sulfides  $\text{C}_n\text{S}$  (with  $n > 1$ )

Carbon oxides  $\text{C}_n\text{O}$  and sulfides  $\text{C}_n\text{S}$  are expected to have singlet ground states for odd numbers  $n$  of carbon atoms, and triplet ground states for even numbers. There are two principal ways to synthesize these molecules in matrices: the thermal or photochemical carbonylation of carbon atoms or molecules  $\text{C}_{n-1}$ , generated by evaporation of graphite with subsequent trapping in low-temperature matrices, or the photolysis or vacuum pyrolysis of suitable precursor molecules, such as diazoketones or thiadiazols.

$\text{C}_2\text{O}$  was prepared either by photolysis of carbon suboxide  $\text{C}_3\text{O}_2$  or by the reaction of carbon atoms and  $\text{CO}$ ,<sup>322a</sup> and characterized by IR, UV-vis, and ESR

spectroscopy in various matrices.<sup>322a,b</sup> The three fundamental vibrations of  $\text{C}=\text{C}=\text{O}$  were observed at 1978, 1074, and 381  $\text{cm}^{-1}$ , and on the basis of isotopic labeling a linear structure was deduced.<sup>322a</sup> This was confirmed by ESR data, which are in accordance with a linear triplet ground state molecule.<sup>322b</sup> The ZFS parameter  $D$  was much depending on the matrix, varying between 0.7392  $\text{cm}^{-1}$  in neon and 0.454  $\text{cm}^{-1}$  in xenon. The decrease of  $D$  in the heavier noble gas matrices was explained by spin-orbit mixing-in of singlet states via the matrix. On annealing matrices containing both  $\text{C}_2\text{O}$  and  $\text{CO}$  at 35 K carbon suboxide was produced, indicating a very low activation barrier for this reaction.<sup>322a</sup>

$\text{C}_3\text{O}$  was synthesized by trapping of carbon atoms with  $\text{CO}$ ,<sup>322c</sup> by FVP of fumaroyl dichloride with subsequent trapping in argon at 10 K,<sup>322d</sup> and by photolysis of  $\text{C}_4\text{O}_2$ , generated from cyclic diazoketones.<sup>323a</sup> Fundamental vibrations of  $\text{C}_3\text{O}$  were observed at 2242.6 ( $\nu_1$ ), 1907.2 ( $\nu_2$ ), and 579.6 ( $\nu_4$ )  $\text{cm}^{-1}$ .<sup>322d</sup> The high frequency of  $\nu_1$  indicates a partial triple bond character of the  $\text{C}-\text{O}$  bond. A small  $\text{C}-\text{C}-\text{C}$  bending force constant (and a rather anharmonic bending potential) was obtained from normal coordinate analysis.

Maier et al. were able to produce  $\text{C}_3\text{S}$  by photolysis of  $\text{OC}_4\text{S}$  (splitting off  $\text{CO}$ ) or  $\text{SC}_4\text{S}$  (splitting off  $\text{CS}$ ) in argon matrices at 12 K.<sup>323b</sup> Fundamental absorptions at 2046.2 ( $\nu_1$ ), 1533.2 ( $\nu_2$ ), and 725.6 ( $\nu_3$ )  $\text{cm}^{-1}$  were in good agreement with the expectation from theory.

$\text{C}_4\text{O}$  is the principal photoproduct (230-nm irradiation) of matrix-isolated  $\text{C}_5\text{O}_2$ .<sup>323c</sup> Intense IR absorptions were found at 2221.7 and 1922.7  $\text{cm}^{-1}$ , and weak absorptions were found at 1431.5, 774.8, and 484.0  $\text{cm}^{-1}$ , as expected from *ab initio* calculations. Maier et al. were also able to generate  $\text{C}_7\text{O}_2$  by flash vacuum pyrolysis of mellitic acid anhydride.<sup>323d</sup> Irradiation of  $\text{C}_7\text{O}_2$  produced a new species with IR absorptions at 2163.8 and 1447.8  $\text{cm}^{-1}$ , which was identified as  $\text{C}_6\text{O}$ .

Mixtures of  $\text{C}_4\text{O}$  and  $\text{C}_6\text{O}$  were also produced by irradiation (405 nm) of matrix-isolated carbon molecules ( $\text{C}_3$  and  $\text{C}_5$ ) in the presence of  $\text{CO}$ .<sup>323e</sup> These carbon oxides were predicted to have triplet ground states, and the observation that they were formed photochemically, but not thermally, was taken as hint for a spin-forbidden reaction between  $\text{CO}$  and (singlet)  $\text{C}_3$  and  $\text{C}_5$ , respectively. The ESR spectra are in accordance with linear triplet ground-state molecules. In neon matrices at 4 K ZFS parameters  $D$  of 0.759 for  $\text{C}_4\text{O}$  and 1.10 for  $\text{C}_6\text{O}$  were observed.<sup>323e</sup>

## E. Heterofunctions at the Carbene C-Atom

A number of carbenes with electronegative substituents, especially halogen and oxygen, have been characterized in matrices, but only a few examples of carbenes with electropositive elements attached to the carbene center are known. Due to the stabilization of an empty carbene p orbital by electron-donating heteroatoms, the ground state of carbenes bearing halogen, oxygen, or other electronegative elements with nonbonding electron pairs at the carbene carbon is singlet. The singlet-triplet gap of heterosubstituted methylene derivatives was the subject of recent *ab initio* studies.<sup>320,321</sup> Electron paramagnetic resonance, a pow-

erful analytical tool in the case of triplet carbenes, is no longer possible, and only vibrational and electronic absorption and emission spectra can be recorded. Thus, in general, higher concentrations of singlet carbenes are necessary for spectroscopic detection. In the 1960s and 1970s, research focused on triatomic halocarbenes, while after 1980, matrix infrared and UV-vis spectra of heterocarbenes with larger organic substituents were reported.

### 1. Triatomic Halocarbenes

Matrix isolation studies of methylene derivatives with one or two halogen substituents cover 10 of the 14 possible structures ranging from CHF to Cl<sub>2</sub>. CHBr, CHI, CICI, and CIBr have not been reported, yet, and Cl<sub>2</sub> was not detected with certainty. The majority of this research was conducted in a few laboratories, especially by the groups of Jacox and Milligan, Andrews, and Bondybey. A variety of experimental techniques were applied, including photolysis of difluorodiazirine,<sup>324</sup> pyrolysis,<sup>325–331</sup> and photolysis<sup>325</sup> of organic and organometallic halides, reaction of alkali metals with halomethanes,<sup>327,331–337</sup> reaction of carbon atoms with halogens<sup>338,339</sup> and hydrogen halides,<sup>340</sup> Ar microwave discharges,<sup>341</sup> and hydrogen<sup>324a,342–350</sup> and noble gas<sup>351–355</sup> resonance VUV photolysis of halomethanes. Also, halomethylenes are byproducts when halomethanes are exposed to excited Ar atoms<sup>356</sup> or proton beam<sup>357–359</sup> irradiation. In some cases structures and valence force potentials were derived from spectroscopic data.<sup>332,336,338,340,342,343,346,349</sup> A table with molecular constants of five dihalocarbenes including ground- and upper-state normal mode frequencies, the (0,0,0–0,0,0) transition, and lifetimes has appeared in ref 344.

Little has been reported on chemical reactions of the triatomic halocarbenes in matrices. Most of the work focuses on physical properties of ground and excited states like vibrational constants and structure parameters. Therefore, only a short summary of the literature and the experimental techniques applied will be given here (Table XV).

CF<sub>2</sub>, in most cases generated from difluorodiazirine<sup>324</sup> or by VUV photolysis of methylene fluoride,<sup>324a,347,354</sup> was the first<sup>341</sup> halocarbene that could be trapped in a matrix, and it is the only dihalocarbene that allows direct IR observation of the bending mode absorption. It was characterized by absorption<sup>324b,324c,328,338,341</sup> and emission<sup>324a,347</sup> spectroscopy. CF<sub>2</sub> does not react with CO<sub>2</sub> or CO under matrix isolation conditions,<sup>324c</sup> but was shown to yield the free-radical CF<sub>3</sub> when reacted with F atoms.<sup>324b</sup> It was also detected after VUV photolysis of methyl fluoride,<sup>343</sup> which was interpreted as the result of the reaction of F atoms with CF. CCl<sub>2</sub> was generated by many different methods including reaction of carbon atoms with chlorine,<sup>339</sup> reaction of alkali metals with halides,<sup>327,335–337</sup> pyrolysis of organometallic compounds,<sup>326,327,329,330</sup> VUV photolysis of methylene chloride<sup>346,348,349</sup> and CCl<sub>4</sub>,<sup>353</sup> and pyrolysis or photolysis of dichloroketene.<sup>325</sup> It was characterized by absorption<sup>325–327,329,330,336,339,349,353</sup> and emission<sup>335,337,346,348</sup> spectroscopy. It was also described as a byproduct in numerous studies dedicated to ions or radicals.<sup>333,352,356–359</sup> In a similar way CBr<sub>2</sub> was characterized by absorption<sup>332,333,357</sup> and emission<sup>337,344</sup> spectroscopy, and was reported as a byproduct<sup>352,353,359</sup> in

**Table XV. IR Spectroscopic Data of Dihalocarbenes, Matrix Isolated in Ar**

	$\nu_1$ , cm <sup>-1</sup>	$\nu_2$ , <sup>a</sup> cm <sup>-1</sup>	$\nu_3$ , cm <sup>-1</sup>	ref(s)
CF <sub>2</sub>	1222	668	1102	324c,338
<sup>13</sup> CF <sub>2</sub>	1191	(665 <sup>b</sup> )	1073	324c,338
CCl <sub>2</sub>	718,721	(326, <sup>c</sup> 333 <sup>d</sup> )	748	336,339,349
<sup>13</sup> CCl <sub>2</sub>	697,700	(325 <sup>c</sup> )	726	336,339,349
CBr <sub>2</sub>	595	(196 <sup>e,f</sup> )	640	332
Cl <sub>2</sub>			535?,525?	331
CHF		1405	1181	343,354,351
<sup>13</sup> CHF		1401	1154	343,351
CDF		1046	1183	343,351
CHCl		1201	806–815 <sup>g</sup>	340,349
<sup>13</sup> CHCl		1197	783–791 <sup>g</sup>	340,349
CDCl			796–805 <sup>g</sup>	340,349
<sup>13</sup> CDCl			778–787 <sup>g</sup>	340
CFCl	1146	(445, <sup>h</sup> 442 <sup>i</sup> )	742,739	342,351
<sup>13</sup> CFCl	1120		718,716	342,351
CFBr	1157	(340 <sup>j</sup> )	647,656,659	351,352
CFI	1121,1133		573,576,583	351
CClBr	739	(257, <sup>k</sup> 260 <sup>l</sup> )	612	326,332

<sup>a</sup> Bending modes ( $\nu_2$ ) derived from electronic spectra are included in parentheses. <sup>b</sup> Reference 354. <sup>c</sup> Reference 335. <sup>d</sup> Reference 348. <sup>e</sup> Reference 337. <sup>f</sup> Reference 344. <sup>g</sup> Quartet. <sup>h</sup> Reference 334. <sup>i</sup> Reference 350. <sup>j</sup> Reference 355. <sup>k</sup> Reference 337. <sup>l</sup> Reference 344.

several other studies. So far no proof of the existence of Cl<sub>2</sub> is available.<sup>331,337</sup> Fluorocarbene CHF<sup>343,351,354</sup> and chlorocarbene CHCl<sup>340,349</sup> were generated by the reaction of carbon atoms with the corresponding hydrogen halides, or by VUV photolysis of organic halides. Polyhalomethanes are suitable photoprecursors of the mixed dihalocarbenes CFCl,<sup>334,342,345,350–352</sup> CFBr,<sup>351,352,355</sup> and CFI.<sup>351</sup> CClBr<sup>326,332,337,344,357,359</sup> was prepared by several different methods including reaction of metal atoms with halomethanes<sup>332,337</sup> and pyrolysis of a mixed phenyl mercury compound.<sup>326</sup> Except for CFI, which was studied by IR only, the mixed dihalocarbenes were characterized by both absorption and emission spectroscopy.

### 2. Aryl- and Alkylhalocarbenes

Owing to the work of Graham<sup>360</sup> in 1965, halodiazirines are now widely used as photochemical precursors of aryl- and alkylhalocarbenes (Scheme XII).

The best-known arylhalocarbene is phenylchlorocarbene<sup>12,79,280,361–366</sup> (193, Chart XIV), whose diazirine precursor is easily synthesized from commercially available benzamidinium hydrochloride. Infrared spectra in Ar matrices<sup>79,280,364,365</sup> as well as UV-vis spectra (Table XVI) in Ar<sup>79</sup> and in organic glasses<sup>12,361,363</sup> of carbene 193 have been published. In the IR-intense absorptions at 1590, 1225, 1170, 848, and 735 cm<sup>-1</sup> were assigned to the carbene.<sup>365</sup> The UV absorptions observed at 307 and 282 nm in an organic glass (3-methylpentane)<sup>361</sup>

**Scheme XII**

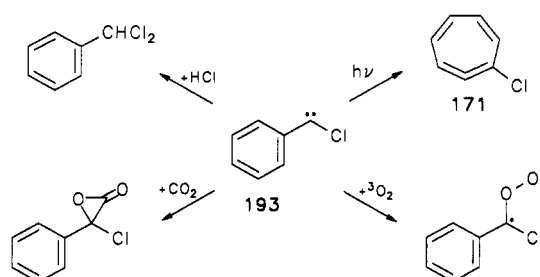
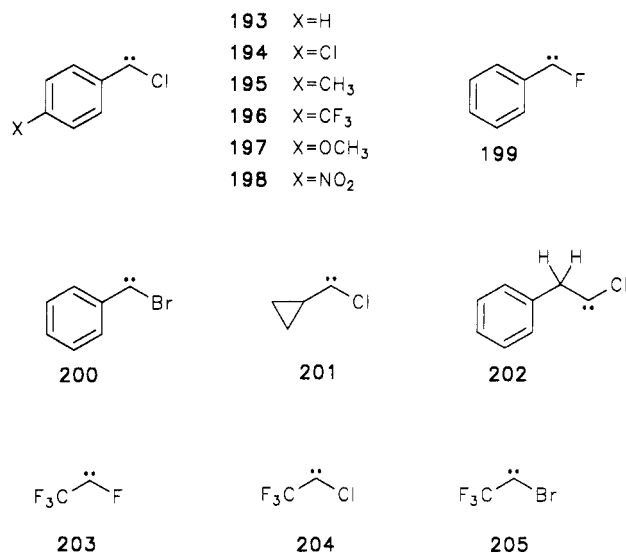


Chart XIV



are shifted to 298 and 276 nm, respectively, in solid Ar.<sup>79</sup> In the ESR no signal was observed, which provides evidence for a singlet ground state. On short wavelength irradiation ( $\lambda > 338$  nm) **193** rearranges to 1-chlorocycloheptatetraene (**171**).<sup>79,280</sup>

The chemistry of carbene **193** in rigid media has been studied quite extensively. In 1982, Tomioka et al. were able to show that the reactivity of **193** toward alcohol and alkenes shows no significant change in glassy matrices at 77 K compared to its ambient temperature chemistry. No increase in H-abstraction products was observed, which was taken as evidence for the carbene's singlet ground state.<sup>362</sup> In an Ar matrix doped with HCl, carbene **193** readily reacted to give benzal chloride on warming to 38 K.<sup>365</sup> In an O<sub>2</sub>-doped Ar matrix the carbene was slowly (6 h at 35 K) transformed to the yellow-green benzoyl chloride O-oxide.<sup>365</sup> This is in contrast to the rapid oxidation of triplet carbenes under the same conditions and reveals the spin restrictions on this reaction.<sup>79</sup> Carbene **193** was also shown to react with CO<sub>2</sub> to produce an  $\alpha$ -lactone in cryogenic matrices.<sup>366</sup>

Phenyl-substituted phenylchlorocarbenes **194**–**197** were isolated in solid 3-methylpentane at 77 K and characterized by their UV-vis spectra (Table XVI).<sup>12</sup> (*p*-Nitrophenyl)chlorocarbene (**198**) was shown to react in doped Ar matrices with O<sub>2</sub> and CO<sub>2</sub> to give the carbonyl oxide and  $\alpha$ -lactone, respectively.<sup>366</sup> The oxidation of **198** is faster, while the carboxylation is slower than the corresponding reactions of **193**, which indicates an electrophilic attack in the former reaction, but that in the latter system a nucleophilic attack of the carbene is rate determining. By comparison of the rates of carboxylation with that of **193** and diphenylcarbene **17** it was shown that it is not the spin state, but rather the philicity of the carbenes that is the rate-determining factor in this reaction.<sup>366</sup>

UV spectra of fluorophenylcarbene (**199**,  $\lambda_{\text{max}}$  270) and bromophenylcarbene (**200**,  $\lambda_{\text{max}}$  328) were recorded in MP glass at 77 K and compared to transient spectra obtained in LFP experiments (Table XVI).<sup>363</sup> Fluorophenylcarbene (**199**) was also identified by IR spectroscopy and shown to rearrange to cycloheptatetraene (**172**) on irradiation in solid Ar.<sup>280</sup>

Table XVI. UV-Vis and IR Spectroscopic Data of Halocarbones (Charts XIV and XV)

carbene	matrix	T, K	UV		IR, cm <sup>-1</sup>	ref(s)
			$\lambda_{\text{max}}$ , nm			
<b>193</b>	Ar	10	300		1590,1225,1170,848	365
<b>193</b>	MP	77	308			361
<b>194</b>	MP	77	323			12
<b>195</b>	MP	77	317			12
<b>196</b>	MP	77	303			12
<b>197</b>	MP	77	346			12
<b>198</b>	Ar	10			1601,1588,1206,831	366
<b>199</b>	MP	77	270			12,363
<b>200</b>	MP	77	328			12,363
<b>201</b>	N <sub>2</sub>	14	460,240	1346,921,852		58
<b>202</b>	Ar	10	304			59
<b>203</b>	Ar	12	465,235	1286,1226,1159,1152		367
<b>204</b>	Ar	12	640,235	1238,1186,1154,920		367
<b>205</b>	Ar	12	665,270,235	1229,1178,1147,858		367
<b>206</b>	N <sub>2</sub>	12	360	1343,1374		372
<b>207</b>	N <sub>2</sub>	20	396	1396		373
<b>208</b>	Ar, N <sub>2</sub>	10	318	1310( <i>s-E</i> ),1300( <i>s-Z</i> )		376
<b>209</b>	N <sub>2</sub>	12	245	1462,1442,603		377
<b>210</b>	Ar, N <sub>2</sub>	10	320	1251( <i>s-E</i> ),1285,1275( <i>s-Z</i> )		378
<b>211</b>	N <sub>2</sub>	10	390	1330,1320,1288,1275		379
<b>212</b>	MP	77	255			381

Cyclopropylchlorocarbene<sup>58</sup> (**201**) was the first alkylhalocarbene to be observed by infrared spectroscopy (see section III.A.2), and in this case no thermal rearrangement (1,2-[H]- or 1,2-[C]-shift) was observed under the conditions applied. When cyclopropylchlorodiazirine was photolyzed in a nitrogen or an Ar matrix at 12 K, **201** was formed in good yield along with the carbon shift product, and the carbene could be thermally trapped with HCl by warming the matrix to 38 K.<sup>58</sup> Rearrangement to chlorocyclobutene occurs—due to the electronic stabilization caused by the cyclopropane ring—only upon irradiation.

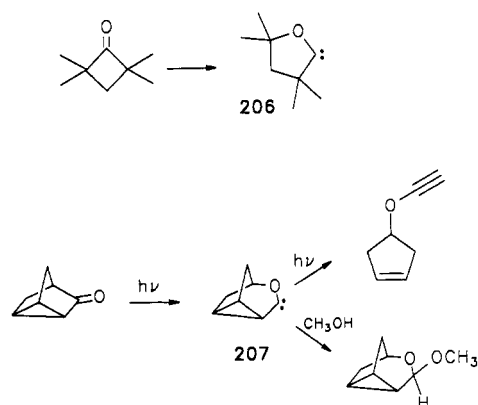
The thermal 1,2-[H]-shift could be followed in the case of benzylchlorocarbene (**202**) and at its isotopomer deuterated at the benzylic positions.<sup>59</sup> In this case the deuterated carbene is stabilized due to a deuterium kinetic isotope effect, and thus much higher concentrations than with the nondeuterated carbene were obtained in an Ar matrix.

The (trifluoromethyl)halocarbenes (**203**–**205**) were subjects of a recent matrix isolation study combined with *ab initio* calculations of infrared and UV-vis spectra (Table XVI).<sup>367</sup> The observed rather long wavelength absorptions in the visible region were taken as evidence for the singlet ground states of these halocarbenes. Broad-band irradiation ( $\lambda > 280$  nm) of the carbenes produced trifluorohaloethenes. In N<sub>2</sub> matrices carbene **205** was found to add N<sub>2</sub> photochemically to form bromo(trifluoromethyl)diazomethane.

### 3. Oxycarbenes

The parent oxycarbene, hydroxycarbene, was suggested as an intermediate in formaldehyde photolysis<sup>368</sup> and in the reaction of carbon atoms with water<sup>369,370</sup> but has never been directly detected. In 1974 a first trace of an oxycarbene UV absorption was reported by Quinkert and co-workers, who photolyzed substituted cyclobutanones in glassy matrices.<sup>371</sup> In the UV, absorptions with maxima around 360 nm were tentatively assigned to the carbenes. These experiments were recently repeated by Matsumura, Ammann, and Sheridan, providing further proof for the oxycarbene formation.<sup>372</sup> Irradiation ( $\lambda = 284$  nm) of 2,2,4,4-tetramethylcyclobutanone, matrix isolated in N<sub>2</sub>,

## Scheme XIII

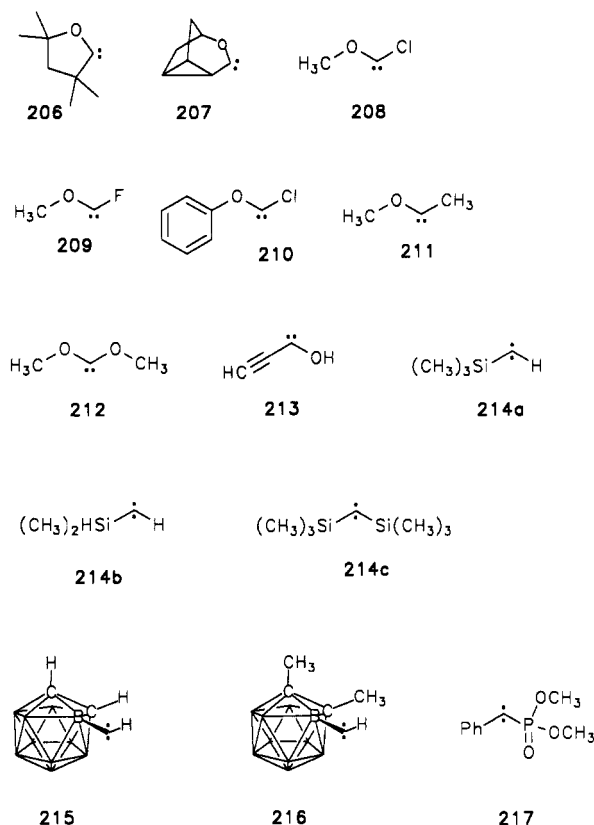


produced carbene 206 with strong IR absorptions at 1343 and 1374  $\text{cm}^{-1}$  and a UV absorption with  $\lambda_{\text{max}}$  of approximately 360 nm. Trapping experiments in organic glasses (MP) containing methanol confirmed this assignment and the earlier experiments of Quinkert et al. Similarly, tricyclic oxycarbene 207 was formed on UV irradiation ( $\lambda = 285$  nm) of nortricyclanone in  $\text{N}_2$  at 20 K.<sup>373</sup> Carbene 207 was characterized by its IR and UV absorptions (Table XVI) and could be trapped by methanol to give the corresponding acetal. Broad band irradiation ( $\lambda > 270$  nm) lead to an increase of nortricyclanone—indicating that the ring expansion of the ketone is reversible—and of a terminal acetylene (Scheme XIII). The ring expansion of cyclobutanones to give oxycarbenes was also the subject of a number of *ab initio* calculations.<sup>372,374,375</sup>

Sheridan et al. described the matrix isolation and characterization of a number of oxygen-substituted carbenes (208–211, Chart XV), generated by photolysis of the corresponding oxydiazirines. All carbenes were isolated in  $\text{N}_2$  or Ar matrices and characterized by IR and UV spectroscopy (Table XVI). Careful analysis of the spectra revealed considerable C–O double bond character and the presence of geometrical isomers in all cases.

Methoxychlorocarbene (208) is a typical example of an oxycarbene, and a vibrational analysis based on isotopic labeling and comparison with chloromethyl methyl ether and methyl chloroformate as model compounds was presented.<sup>376,413</sup> On  $^{18}\text{O}$ -labeling, two IR absorptions (at 1300 and 950  $\text{cm}^{-1}$ , respectively) exhibited large isotopic shifts, and were assigned to the antisymmetric and symmetric C–O–C stretching mode of the *cis*-carbene, indicating the partial double bond character of the C–O bond. A strong absorption at 690  $\text{cm}^{-1}$  was assigned to the C–Cl stretching mode. A second set of absorptions at 1310 and 774  $\text{cm}^{-1}$  exhibited a different wavelength dependence of the photochemistry and was assigned to the *trans*-carbene.<sup>376</sup> Irradiation at 370 nm caused more rapid destruction of the *trans*-carbene, while upon 290-nm irradiation the *cis*-carbene was more rapidly photolyzed. The principal photoproducts of 208 in Ar were acetyl chloride, ketene, and HCl, while in  $\text{N}_2$  traces of methyl chloride and CO were also observed. This is in contrast to the room temperature decomposition of the carbene which produces mainly methyl chloride and CO. More evidence for carbene 208 was provided by trapping experiments with HCl, which produced dichloromethyl methyl ether,

## Chart XV



and from the direct IR observation of the dimerization of 208 in MP glass at 80 K.

Geometrical isomers, indicating significant double bond character for the C–O bond, were also observed for methoxyfluorocarbene (209),<sup>377</sup> phenoxycarbene (210),<sup>378</sup> and methylmethoxycarbene (211).<sup>379</sup> On further irradiation, these carbenes rearrange to the corresponding carbonyl compounds, accompanied by loss of CO and hydrogen halide.

Methylmethoxycarbene (211) is one of the few carbenes bearing  $\alpha$ -H atoms that could be characterized in low-temperature matrices. The carbene could be trapped in a methanol/2-methylbutane glass at temperatures as high as 80 K, which is in accord with *ab initio* calculations<sup>380</sup> predicting a barrier of more than 20 kcal  $\text{mol}^{-1}$  for the [1,2]-H-shift in (alkyloxy)carbenes. Photolysis ( $\lambda > 340$  nm) of 211 in an  $\text{N}_2$  matrix produced acetone (product of methyl shift), methyl vinyl ether (product of H-shift), ketene, and methane, the latter formed by fragmentation and rearrangement.<sup>379</sup> Dimethoxycarbene (212) was spectroscopically characterized by its UV-vis absorption in a MP glass at 77 K (Table XVI).<sup>377,381</sup>

Hydroxyethynylcarbene (213) and its  $^{18}\text{O}$ -isotopomer were produced by the reaction of  $\text{C}_3$  carbon clusters with matrix-isolated water and characterized by IR spectroscopy ( $\text{C}\equiv\text{C}$  stretching mode at 1992.8 and 1999.8  $\text{cm}^{-1}$ ).<sup>382</sup> Photolysis of the carbene caused isomerization to propynal.

## 4. Heterocarbenes with Electropositive Substituents

In contrast to the rich chemistry of carbenes bearing electronegative substituents, only few carbenes with electropositive substituents have been investigated experimentally. The photochemistry of (trimethylsi-

Table XVII. ESR Data of Silylcarbenes and Carboranylcarbenes

carbene	matrix	T, K	D/hc, cm <sup>-1</sup>	E/hc, cm <sup>-1</sup>	E/D	ref
214a	Ar	4	0.613	0.00145	0.002	383b
214b	Ar	4	0.628	0	0	383b
214c	Ar	4	0.614	0.00252	0.004	383b
215	MCH	10	0.657	<0.002	<0.003	385b
216	MCH	10	0.661	<0.002	<0.003	385b
217	Ar	10	triplet			386

lyl)diazomethane in Ar matrices was reported by both Chapman et al.<sup>383a</sup> and Chedekel et al.<sup>383b</sup> 2-Methyl-2-sila-2-butene (1,1,2-trimethylsilene) was the principal product characterized, while (trimethylsilyl)carbene (214a) was not detected by IR spectroscopy. Attempts to trap 214a with molecular oxygen also failed,<sup>384</sup> which indicates that the carbene is either short-lived under the conditions of matrix isolation—which we feel is unlikely—or does not survive photolysis of the diazo precursor. Irradiation with short wavelength UV light (250 nm) finally produced dimethylvinylsilane.<sup>384</sup>

Although these IR experiments did not provide direct evidence for the formation of carbene 214a, an ESR spectrum typical of a ground-state triplet carbene could be obtained in solid Ar (Table XVII).<sup>383b</sup> This means that at least small amounts of the carbene are formed and are stable in the matrix. Similarly, ESR spectra of dimethylsilylcarbene (214b) and bis(trimethylsilyl)carbene (214c) were recorded (Table XVII).<sup>383b</sup> From the very small *E* values a linear structure of  $\alpha$ -silylcarbenes was deduced, which was rationalized by an  $p_\pi$ - $d_\pi$  overlap between the carbene carbon and adjacent silicon atom.

3-*o*-Carboranylcarbenes 215 and 216 are the first boron-substituted carbenes that have been characterized spectroscopically.<sup>385</sup> Trapping experiments in solution provided evidence that 216 is a triplet ground state carbene with enhanced triplet activity.<sup>385a,c</sup> This was confirmed by the observation of a linear Curie plot in the ESR for both 215 and 216 over the range 14–30 K.<sup>385b</sup> The small ZFS parameter *E* was taken as evidence for a linear structure of both carbenes (Table XVII), in accordance with semiempirical MNDO calculations.

The isolation of phosphonylphenylcarbene (217) in Ar at 10 K was recently reported by Tomioka et al.<sup>386</sup> IT absorptions at 1268, 788, and 536 cm<sup>-1</sup> were assigned to the carbene. Carbene 217 proved to be very photostable, compared to other phenylcarbenes and did not rearrange to a cycloheptatetraene even under prolonged short wavelength UV irradiation. Annealing of O<sub>2</sub>-doped matrices at 35 K readily produced the carbonyl oxide while the formation of the ketene in CO-doped matrices at the same temperature was considerably slower. This behavior was also observed with other triplet carbenes and attributed to spin restrictions in formal “spin-forbidden” reactions.

In a series of papers Bertrand et al. described the synthesis of stable phosphinosilylcarbenes, which can be formulated both as  $\lambda^3$ -phosphinocarbenes or as  $\lambda^5$ -phosphaacetylenes.<sup>387a-c</sup> *Ab initio* calculations on the parent compound suggest that the electronic structure is properly described as  $\lambda^5$ -phosphaacetylene, although there are some low lying triplet carbene states.<sup>387d</sup> Thus, this class of compounds will not be discussed further in this review.

## IV. Reactions of Carbenes in Matrices

Matrix isolation spectroscopy is frequently used for the direct observation of reactions and in some cases for the determination of kinetic data. An excellent review on reactions of triplet carbenes in low-temperature glasses and solids—with emphasis on ESR spectroscopy as the analytical tool—was presented by Platz in 1990.<sup>8</sup> Here, a summary of classes of carbene reactions in matrices (emphasis on inert gas matrices) is given, only, while special carbene reactions are treated in the chapters of individual carbenes.

A difficulty inherent to solid-state conditions is that generally a distribution of species in matrix sites with slightly differing spectroscopic as well as kinetic properties is formed, which results in a distribution of rate constants. This is reflected in nonexponential kinetics of first and pseudo-first-order reactions which makes it difficult—if not impossible—to extract meaningful reaction rates from kinetic data. “It would appear that solid-state ESR kinetic studies of unimolecular reactions of triplets will reveal more about environmental factors than about the desired reaction” and “the chemistry of singlet...[carbene]...may be entirely predestined by the local matrix site.”<sup>388a</sup> This excerpt from a 1983 publication by Tomioka, Platz, and co-workers on the solid-state chemistry of 1,2-diphenylpropylidene<sup>388b</sup>—which was already cited by Chapman et al.<sup>57</sup>—illustrates well the difficulties which have to be faced when solution conditions no longer apply. Despite many attempts to deduce reliable information from this kind of disturbed kinetics<sup>10,389-391</sup> the data should be treated with great care. For bimolecular reactions—where diffusion of the reactants in the solid state is important—it is generally impossible to obtain reliable kinetic data.

### A. Intramolecular Reactions

Some theoretical investigations of carbene rearrangements involving carbon or hydrogen migration have been published. These include a few *ab initio* studies,<sup>52,380,392,393</sup> and a larger number of semiempirical and qualitative investigations.<sup>394-400</sup> For further references see Evanseck and Houk.<sup>52,380</sup>

#### 1. Hydrogen Shifts

Alkylcarbenes bearing  $\alpha$ -hydrogens undergo rapid thermal 1,2-[H]-shift to yield the corresponding olefins. At ambient temperature in dilute solution, this reaction determines the lifetime of these carbenes in many cases. Typical rate constants are in the range of 10<sup>6</sup> to 10<sup>8</sup> s<sup>-1</sup>, with activation energies of about 1–5 kcal/mol and relatively low pre-exponential factors of 10<sup>8</sup>–10<sup>11</sup> s<sup>-1</sup>.<sup>401,402</sup>

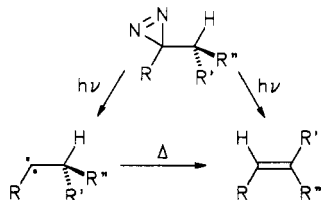
Although precursor photolysis in matrix isolation experiments takes place at temperatures as low as 4–10 K, direct observation of the thermal rearrangement is often difficult to achieve due to the relatively low time resolution of these experiments (minutes) and the possibility of thermally excited “hot” carbenes to rearrange during precursor photolysis and/or rearrangements from excited states of the precursor.

The first thoroughly conducted kinetic analysis of intramolecular hydrogen shift reactions of ground-state triplet carbenes in matrices (the *o*-tolylcarbene to *o*-xylylene 1,4-[H]-shift and the phenylmethylcarbene



to styrene 1,2-[H]-shift) was published by McMahon and Chapman in 1987.<sup>57</sup> Matrix isolation of benzylchlorocarbene (**202**) allowed the observation of the thermal hydrogen shift of a ground state singlet carbene.<sup>59</sup> While phenylmethylcarbene (**56**) (triplet ground state) was found to be stable at 10 K, **202** (singlet ground state) was not, which might indicate the influence of the spin state on carbene rearrangements.

In a number of cases the carbene could not be detected, i.e. only the hydrogen rearrangement products were present in the matrix after photolysis of the precursor. This was the case after decomposition of 1-(4-methoxyphenyl)diazethane<sup>57</sup> and 8-methyl-1-naphthyl diazomethane,<sup>129-131,133</sup> where the H-shift leads to a biradical. In these cases the intermediacy of the carbene could not be established by matrix spectroscopy. Most probably, there is a pathway from an excited state of the precursor directly to the olefin.



## 2. Migration of Alkyl and Aryl Groups

Although the rigidity of a matrix environment hinders migration of larger groups and thermal rearrangements of this kind could not be observed so far, photochemical carbon shifts are frequent. Photolysis of carbene precursors often results in the formation of rearranged products (see above). It was shown that phenyl migration during photolysis of 1,2-diphenyl-1-diazopropane becomes predominant over concurrent H-migration when the reaction temperature is lowered, but is almost completely eliminated in the solid state.<sup>388</sup> No phenyl migration at all was observed after photolysis of benzylchlorodiazirines, which are precursors of singlet carbenes, and it was concluded that phenyl migration is a reaction of the triplet state.<sup>403</sup>

## 3. Other Rearrangements

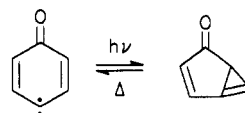
Important carbene rearrangements that have been investigated in matrices are the Wolff rearrangement, the ring expansion of phenylcarbenes to cycloheptatetraenes, and the vinylcarbene-cyclopropene rearrangement.

The Wolff rearrangement (Scheme III) has synthetic as well as technical applications and therefore was target of several studies (see section B). Although the kinetics of disappearance of  $\alpha$ -ketocarbenes was reported several times, data obtained by ESR are not very reliable, because the formation of diamagnetic products can principally not be observed. Thus it is not possible to discriminate between rearrangement and intermolecular pathways (dimerization, reaction with the organic glass, etc.). IR spectroscopy is the method of choice to observe both the carbenes disappearing and the newly formed ketenes growing in. The only ketocarbenes that have been characterized by IR spectroscopy were Chapman's carbenes **120**–**122**<sup>207,208</sup> and Tomioka's carbene **123**.<sup>209</sup> Unfortunately, no thermal rearrangement

was observed in these cases, and therefore no kinetic data could be obtained.

The photochemical ring enlargement of phenylcarbenes to cycloheptatetraenes has been studied by Chapman et al.<sup>72,76,279-281</sup> and is described in sections III.A.3 and III.C.5 (Scheme IX). Under FVP conditions phenylcarbenes thermally rearrange and cycloheptatetraenes are trapped, but the barriers toward rearrangement are high enough to prevent thermal rearrangement in inert gas matrices at low temperatures, and thus kinetic studies could not be conducted.

The kinetics of a cyclopropene-vinylcarbene rearrangement has been studied by our group.<sup>269,270</sup> A curved Arrhenius plot was observed, and at temperatures below approximately 20 K the rates of this rearrangement became independent of temperature.<sup>269</sup> This was taken as evidence for a quantum mechanical tunneling mechanism (heavy-atom tunneling). Evaluation of the kinetic data using a modified Arrhenius equation according to Bell<sup>404</sup> gave an activation barrier in the order of 2.5 kcal/mol (depending on the matrix) and a tunneling distance of 0.4 Å under the assumption of a mass of 12 (carbon atom) tunneling. At 10 K the rates of rearrangement depend much on the matrix and in Kr are 5 times and in Xe 37 times faster than in Ar. Together with the observed very small Arrhenius preexponential factors *A* this observation suggests that the rate-determining step of the rearrangement involves the ISC and the singlet cyclopropene directly rearranges to the triplet carbene in a formally spin-forbidden reaction.



## B. Intermolecular Reactions

### 1. Atom Abstractions and Insertion Reactions

Intermolecular atom abstraction to produce radical pairs is one of the most important reactions of triplet carbenes, and H atom transfer is the dominant decay process of carbenes in organic glasses.<sup>289,388a</sup> H- and Cl-abstractions have been extensively studied by ESR spectroscopy and reviewed by Platz several times,<sup>8,10</sup> and therefore only a brief summary will be given here.

Pseudo-first-order Arrhenius parameters for diphenylcarbene (**17**) in a variety of organic glasses (e.g. benzene, toluene, cyclohexene, and the deuterated counterparts) were reported. ESR signals were produced by brief photolysis of diphenyldiazomethane, and the decay of signal intensity is followed immediately afterward.<sup>10</sup> *E<sub>a</sub>* varied between 2.1 (toluene) and 3.2 kcal/mol (cyclohexene), the Arrhenius preexponential factor *A* was very small (log *A* between 2.1 and 4.3), and a pronounced kinetic deuterium isotope effect was observed.<sup>405,406</sup> On the basis of these experiments, quantum mechanical tunneling (QMT) was proposed as mechanism for H-abstraction. This was supported by the observation that **17** was completely stable in carbon tetrachloride at 77–100 K, which implies that chlorine, in contrast to hydrogen, is not abstracted by a QMT mechanism.<sup>407</sup> Similar observations were

reported for other triplet carbenes such as fluorenylidene (136) or dibenzocycloheptatrienyli-  
dene (179).<sup>10,407</sup> Platz et al. were able to measure both the decay of the triplet signal intensity of 136 and dibenzocyclohepta-  
dienylidene 181 in organic glasses at 77 K as well as the formation of triplet radical pairs as primary products of the H transfer.<sup>289</sup>

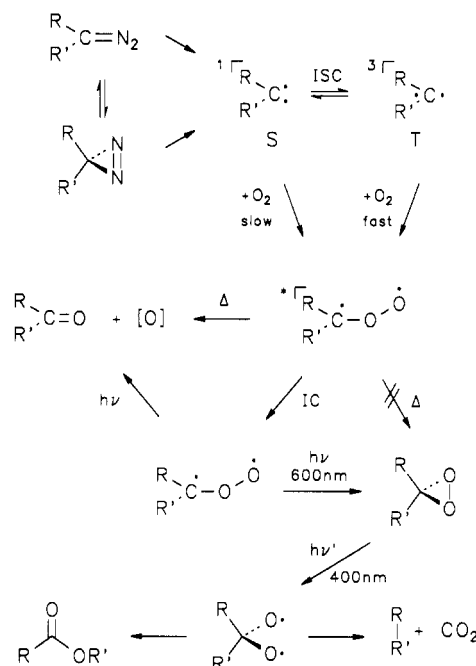
One problem with experiments in organic glasses is secondary photolysis, if the photochemical generation of carbenes and subsequent thermal reactions are not rigorously separated.<sup>408</sup> Many carbenes are long-lived enough even in reactive matrices such as frozen alcohols to become electronically excited during photolysis of the precursor. Electronically excited carbenes are expected to exhibit a very different chemical behavior compared to the ground-state carbenes. Thus triplet diphenylcarbene (17), generated by irradiation of diphenyldiazomethane in frozen alcohols at 77 K, produces mainly ethers, the products of formal OH-insertion, in a thermal reactions. Alcohols, the products of the formal CH-insertion, are photoproducts rather than thermal products.<sup>408</sup> It was also shown that triplet fluorenylidene (136) is less sensitive to secondary photolysis.

In doped inert gas matrices with an excess of inert gas (200:1 to 10:1 excess) the generation of the carbene is in most cases separated from the thermal intermolecular reaction by a diffusion step. This allows one to first characterize the carbene in its ground state at temperatures below 12 K, and then induce the thermal reaction by annealing the matrix above 20–30 K. Typical ratios of carbene/reagent/inert gas are 1:10:1000. So far, H-abstractions in doped inert gas matrices have not been reported, but intermolecular reactions of carbenes with small molecules are frequently investigated in this type of matrix.

## 2. Reactions with Oxygen

The oxidation of carbenes with molecular oxygen is now fairly well understood and frequently used to identify matrix-isolated carbenes.<sup>28,409</sup> Both singlet and triplet carbenes give carbonyl *O*-oxides (Criegee intermediates) as primary adducts upon annealing (30–40 K) of O<sub>2</sub>-doped inert gas matrices. Carbonyl oxides are easily identified by their strong  $\pi \rightarrow \pi^*$  absorption in the visible region (in most cases the matrix turns intense yellow to red) and by their intense O–O stretching vibration around 900 to 1000 cm<sup>-1</sup>.<sup>28</sup> Carbonyl oxides are extremely photolabile and irradiation with red light (600 nm) rapidly produces dioxiranes (Scheme XIV). The dioxiranes are stable under these conditions but at 400-nm irradiation are converted to esters or lactones. In several cases CO<sub>2</sub> was observed as a byproduct of this photochemistry. The sequence carbonyl oxide–dioxirane–ester is easily followed spectroscopically and highly characteristic for matrix-isolated carbenes in O<sub>2</sub>-doped matrices. Singlet carbenes such as phenylchlorocarbene (193) are oxidized several orders of magnitude more slowly than triplet carbenes. The same difference in reactivity was also observed in solution at room temperature using LFP and nanosecond time resolution.<sup>410</sup> The more electron-deficient (*p*-nitrophenyl)chlorocarbene (198) reacts markedly faster both in matrix<sup>366</sup> and in solution,<sup>410</sup> indicating an electrophilic attack of the carbene on the O<sub>2</sub> molecule.

## Scheme XIV



An interesting observation reported first by Wasserman et al. was the emission of a strong chemiluminescence during warmup of organic glasses containing diphenylcarbene (17)<sup>68</sup> or bis(trifluoromethyl)carbene (7)<sup>63</sup> and traces of oxygen. The mechanism leading to chemiluminescence was later investigated by Turro et al.<sup>139</sup> Following the carbene concentration in O<sub>2</sub>-doped freon glasses at temperatures >77 K by ESR and fluorescence spectroscopy, and simultaneously measuring the chemiluminescence spectra and intensity, revealed that chemiluminescence decay was faster than consumption of the carbenes. In all cases the chemiluminescence was identified as phosphorescence of the corresponding carbonyl compounds. From these experiments oxygen transfer from carbonyl oxides to carbenes, leading to carbonyl compounds in electronically excited states, was proposed as the step leading to emission of light.

In a similar experimental setup we could show that in O<sub>2</sub>-doped Ar matrices chemiluminescence starts at temperatures as low as 15 K.<sup>73,74,79,411</sup> Again, chemiluminescence decay was faster than oxidation of the carbenes, but IR spectroscopy excluded carbonyl oxides as oxygen-transfer reagents. The direct reaction of oxygen atoms (produced by decomposition of carbonyl oxides) with carbenes, producing a C=O bond in situ in a very exothermic reaction, was now proposed as chemiluminescent step (Scheme XIV).

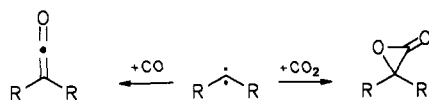
## 3. Other Intermolecular Reactions

Dimerization of carbenes is an important reaction in solution, but in matrices due to the slow diffusion of larger molecules it is only rarely observed. The dimerization of methylene was reported by Milligan and Pimentel (Scheme I).<sup>1</sup> Other dimerizations which have been observed directly are that of cyclopentadienyli-  
dene (133),<sup>29,228,412</sup> methoxycarbenes 208<sup>413</sup> and 212,<sup>381</sup> and of bis(trifluoromethyl)carbene (7, Scheme II).<sup>64</sup>

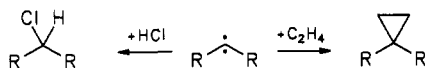
The carbonylation of carbenes produces ketenes, which are easily identified by IR spectroscopy. This

reaction is generally slower than the oxidation with  $O_2$ , and higher concentrations of CO (2–5%) than  $O_2$  (<2%) are required to get comparable yields of products on annealing the matrices. In most cases the appearance of a new IR absorption in the range 2000–2200  $cm^{-1}$  is taken as evidence for the formation of a ketene. As long as the ketene has not been identified by direct comparison with the authentic matrix isolated ketene, this has to be taken with some caution. Several triplet carbenes were characterized by CO trapping: methylene,<sup>2</sup> methylcarbene (1),<sup>53</sup> 3-pyridylcarbene (53),<sup>136</sup> bis(trifluoromethyl)carbene (7),<sup>64</sup> cyclopentadienylidene (133) and derivatives,<sup>29,234</sup> 4-oxo-2,5-cyclohexadienylidene (158),<sup>264</sup> and cycloheptatrienylidene (169). (See discussion in section III.C.5 about the identification of this carbene.<sup>282</sup>)

The formally spin-allowed carbonylation of singlet carbenes should be faster, but so far dicyclopropylcarbene (3) is the only singlet carbene that has been trapped with CO.<sup>56</sup>



Carboxylation of carbenes leads to  $\alpha$ -lactones (oxiranones), which are not easily accessible by other methods. The parent  $\alpha$ -lactone was produced by irradiation of diazomethane in solid  $CO_2$  at 53 K (Scheme I).<sup>45</sup> Comparison of the rates of carboxylation of diphenylcarbene (17), phenylchlorocarbene (193, Scheme XII), and (*p*-nitrophenyl)chlorocarbene (198) revealed that this reaction is not governed by the spin multiplicity, but rather by the philicity of the carbene, and nucleophilic attack of the carbene at the  $CO_2$  carbon atom is rate determining.<sup>366</sup>



HCl trapping is frequently used to provide chemical evidence for the formation of singlet carbenes in matrices.<sup>58,365,376</sup> The chlorides formed are generally stable molecules which can be matrix isolated independently to compare the spectra. Kinetic data relating to this reaction have not been reported.

The direct observation of the reaction of a carbene and ethylene was reported by Mal'tsev et al.<sup>233,412</sup> Annealing of a 2% ethylene-doped argon matrix containing cyclopentadienylidene (133) at 40–45 K produced [2.4]spiro-4,6-heptadiene.

## V. Conclusions

Matrix isolation spectroscopy is now a well-established technique for the determination of spectroscopic as well as chemical properties of carbenes. Numerous carbenes are completely stable under these conditions—especially in inert gas matrices—and can be characterized with routine spectrometers available in most laboratories. Although a wealth of spectroscopic data of more than 200 carbenes has been published during the years, due to the limited number of spectroscopic methods applicable to solid-state matrices, important information is still lacking. Structures of carbenes have been deduced from ESR data. The

information obtained by this method is limited basically to the bond angle at the carbene center, it has to be taken with some care, and is not available for singlet carbenes. Thus, the determination of structural data of carbenes is a rewarding goal for future research. A practical approach to this might be the use of oriented matrices using photoselection or solid-state NMR techniques. Another field which is still underdeveloped is the direct observation of reactions in matrices. Some reactions like the oxidation with molecular oxygen are now frequently used, but the number of reactions which could lead to new and fascinating molecules and provide insight into details of mechanisms which are not available by other methods is almost only limited by imagination.

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