CARBENES IN THE SYNTHESIS OF HETEROCYCLES (REVIEW)

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The syntheses of heterocyclic compounds by reactions of carbenes with carbon–heteroatom multiple bonds, isomerization of unstable adducts of carbenes to carbon–carbon bonds, and the incorporation of carbenes in C–H, C–N, and C–O bonds are examined.

The branch of organic chemistry that is concerned with the study of the behavior of unstable derivatives of divalent carbon has been undergoing intensive development in recent years [1, 2]. Carbenes have received practical application in the syntheses of various classes of organic compounds [3-5].

The possibilities of the application of reactions of carbenes for the preparation of heterocyclic systems are examined in the present review. The following types of reactions that yield heterocycles can be singled out; 1) the addition of carbenes to carbon–heteroatom multiple bonds, 2) the addition of carbenes to carbon–carbon multiple bonds accompanied by opening of the three-carbon ring with the formation of a heteroring, 3) intramolecular incorporation of carbenes in C=C bonds or in C–H, C–N, and C–O single bonds.

The high heat content of carbene particles explains their high reactivity and their possibility of giving structures that have a large supply of potential energy, for example, in the form of angular strain energy. The addition of carbenes to multiple bonds leads to the formation of three-membered rings. These reactions are characterized by a low activation barrier (less than 5 kcal/mole) and low exothermicity. In connection with the fact that the heat effect for the addition process is high (up to 90 kcal/mole), the formation of products of isomerization of the "hot" cyclic adducts is observed to an appreciable extent when the reaction is carried out in the gas phase. As a rule, isomerization does not occur in the liquid phase as a result of effective "cooling" of these adducts by solvent molecules.

Skell [6] has proposed that the mechanism of the reaction of a carbene with a multiple bond depends on the multiplicity of the particle – a singlet carbene adds in one step and stereospecifically, whereas a triplet carbene adds in two steps and nonstereospecifically. The presence of a sextet of electrons on the carbene C atom is responsible for the electrophilic properties of carbenes. In fact, those unsaturated compounds that contain electron-donor substituents attached to a multiple bond give products in highest yields and at highest relative reaction rates on reaction with carbenes.

The Addition of Carbenes to Carbon – Heteroatom Multiple Bonds

In contrast to the carbon–carbon bond, the carbon–heteroatom multiple bond is polar, and the heteroatom is the negative end of the dipole, and the carbon atom is the positive end of the dipole. When unshared electron pairs are present on the heteroatom, the reaction of carbenes with these bonds may lead to the formation not only of heterorings but also to isoelectronic acyclic molecules – ylids. The latter can subsequently undergo ring closure to a heteroring or undergo a 1,3-cycloaddition reaction. In addition, the reactions of carbenes with carbon–heteroatom multiple bonds sometimes are complicated by parallel processes associated with the ability of these bonds to add nucleophilic reagents, for example carbene precursors – aliphatic diazo compounds and trihalomethyl anions.

Addition to the Carbon–Nitrogen Bond. The reaction of carbenes with the C=N bond, which leads to aziridines, has been investigated in greatest detail. It was first studied in the case of the reaction of dichlorocarbene with benzylideneanilines [7]. The reactions of more than 15 ring-substituted benzylideneanilines and aliphatic-aromatic azomethines with dichlorocarbene, generated by the action of potassium or sodium alkoxides on chloroform, hexachloroacetone, or ethyl trichloroacetate, were subsequently studied in [8-18]. The yields of 3,3-dichloro-1,2-diarylaziridines depend not only on the experimental conditions but also on the nature of

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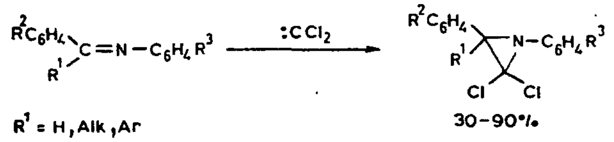
substituents attached to the C = N bond. The aziridines are formed via the carbene pathway [10, 17] rather than by addition of the trichloromethyl anion, which is the dichlorocarbene precursor, to the C = N bond with subsequent closing of the anion to a heteroring. The introduction of donor substituents into the aromatic ring increases the rate of formation of the aziridine, whereas the introduction of acceptor substituents reduces the rate. However, the preparative yields of aziridines with donor substituents in the ring are lower then expected from a comparison of the relative reactivities of the azomethines. This is associated with the fact that gem-dichloroaziridines that contain electron-donor groups attached to the ring readily undergo thermal isomerization or react with nucleophilic reagents (water, alcohol) with ring closure.

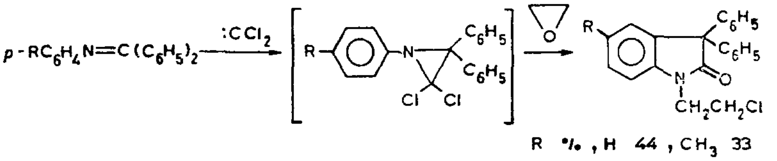


Rather than an aziridine, its hydrolysis product – 1,3-di-tert-butylaziridinone – was obtained in the reaction of dichlorocarbene, formed from chloroform and potassium tert-butoxide, with N-neopentylidene-tert-butylamine [19]. Under these conditions, other aliphatic Schiff bases give only condensation products.

A two-phase method for the synthesis of gem-dichloroaziridines, which includes generation of the carbene from chloroform and 50% aqueous sodium hydroxide in the presence of quaternary salts of ammonium bases, was recently extended [20-23]. Aziridines containing a nitro group in one of the aromatic rings [21, 22] and 1-isopropyl-2-tert-butyl-3,3-dichloroaziridine [21] were obtained in higher than 70% yields by this method.

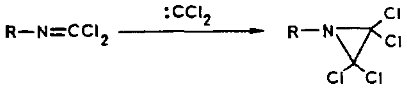
1-(2-Chloroethyl)-3,3-diphenyloxindoles, the formation of which was shown to occur through the aziridine [24], were isolated in the reaction of benzophenone anils with dichlorocarbene, obtained from chloroform and ethylene oxide in the presence of a tetralkylammonium salt.

Attempts to obtain an aziridine from aromatic and aliphatic azomethines and dichlorocarbene, formed by heating trihalomethyl derivatives of mercury [25] (the Seyferth method) or sodium trichloroacetate [19], were unsuccessful, and this was linked with the thermal instability of dihaloaziridines [12-14, 26, 27].



N-(1-phenyl-1-propenyl)dichloroazomethane (60%), probably formed by thermal isomerization of the intermediate azabicyclobutane as in the case of butadienes from bicyclobutanes [29], was isolated in the reaction of 3-methyl-2-phenylazirine and dichlorocarbene, generated from phenyltrichloromethylmercury [28].

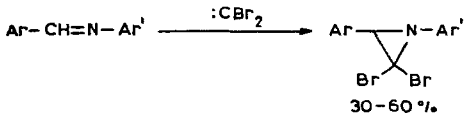
The Seyferth method [30] is suitable for the synthesis of aziridines that contain no less than three chlorine atoms attached to the ring. Thus the corresponding aziridines were obtained in the reaction of phenyldichlorobromomethylmercury with carboimidoyl dichlorides.



R = $i\text{-}C_3H_7$ (43%); C_6H_{11} (29%); C_6H_5 (53%)[25,31]; $p\text{-}CH_3C_6H_4$ (78%);
$o\text{-}ClC_6H_4$ (54%)[31]; $(C_2H_5O_2C)_2N$ (25%)[32,33]

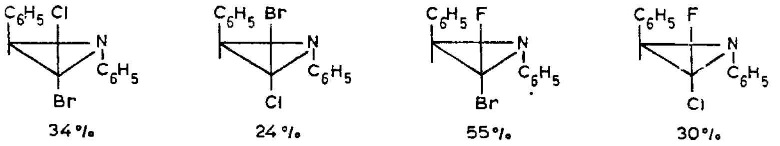
The reaction of azoarenes, azoxyarenes [31], and aryl isocyanates [34] with phenyldichlorobromomethylmercury initially gives N-aryldichloroimines, which are subsequently converted to N-aryltetrachloroaziridines.

Dibromocarbene, formed from bromoform and potassium tert-butoxide, adds to benzylideneanilines to give 3,3-dibromo-1,2-diarylaziridines [27, 35-37].



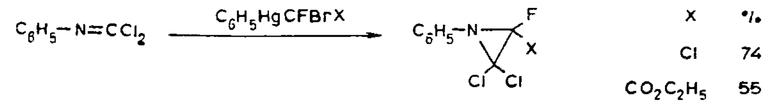
The addition of chlorobromo-, fluorochloro-, and fluorobromocarbenes, generated by the action of bases on trihalomethanes, to benzylideneanilines proceeds stereoselectively to give, in the case of chlorobromocarbene, a mixture of isomers, whereas one stereoisomer is formed in the case of fluorine-containing carbenes.

The thermodynamically less-stable aziridine stereoisomer in which the lower halogen atom is oriented in the syn position relative to the unshared pair of nitrogen is preferably formed [37]. Bromine- and fluorine-containing aziridines are thermally less stable than the corresponding chloroaziridines, and their yields are therefore lower than those of the latter.

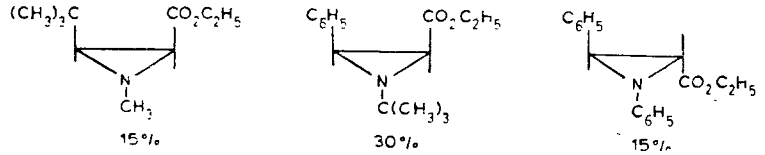


According to the data in [10], chlorocarbene also reacts stereoselectively with benzylideneaniline to give cis-3-chloro-1,2-diphenylaziridine.

Fluorochloro- and fluorocarbethoxycarbenes, obtained by heating the corresponding organomercury compounds, add to N-phenyldichloroimine to give fluorine-containing aziridines [38, 39].

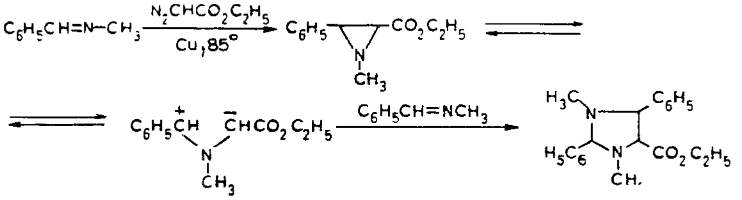


Thermal catalytic and thermal and photochemical decomposition of diazoacetic ester in the presence of imines lead to carbethoxyaziridines only in the first case [40].

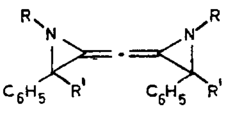


In the case of the reaction with benzylideneaniline, 3-anilinocinnamate, which was previously isolated as the only product of the same reaction [41], was obtained along with the aziridine. It was also established that the aziridine is not converted to the cinnamate under the reaction conditions. In all cases the aziridines have the most stable trans configuration for 1,3-diphenyl-2-carbethoxyaziridine, whereas they have the cis configuration in the remaining cases.

An imidazolidine was isolated in 40% yield in the reaction of diazoacetic ester with N-benzylidenemethylamine [40]. The imidazolidine is formed through the intermediate aziridine, which undergoes ring opening on heating to the azomethine ylid, which then reacts as a 1,3-dipole with the polarized C = N bond of the starting azomethine.

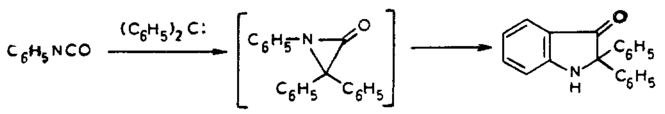


The formation of allenes with the following structure was established in the reaction of the simplest dicarbene — the C_3 molecule — with imines [42]:

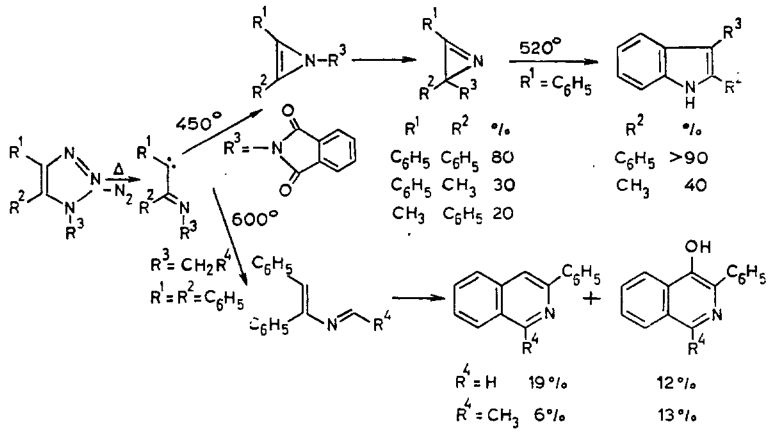


$R = i\text{-}C_3H_7,\ C_3H_7;\ R' = H,\ C_6H_5$

The photolysis of diphenyldiazomethane in the presence of phenyl isocyanate leads to 2,2-diphenylindoxyl (in 15% yield) [43]. The authors propose that the diphenylcarbene obtained during the photolysis of the diazo compound adds to the C = N bond, after which the α-lactam undergoes two [1, 7] sigmatropic shifts. The corresponding 3-phenylbenzoxazolone was obtained in 32% yield as a result of 1,3-cycloaddition to the C = N bond of phenyl isocyanate of a ketocarbene obtained from 3,4,5,6-tetrachloroquinone diazide [44].

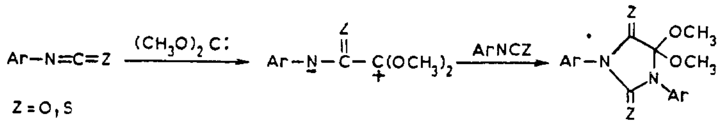


The pyrolysis of 1,2,3-triazoles, which proceeds with the formation of iminocarbenes, may lead, depending on the nature of the substituents and the experimental conditions, to 2H-azirine, indole [45], and isoquinoline [46] derivatives.

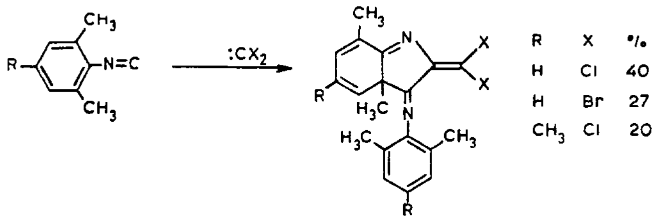


Photolysis of 3-allyl-2H-aziridines gives iminocarbenes, which undergo intramolecular cyclization to 2-azabicyclo[3.1.0]-2-hexane derivatives [47].

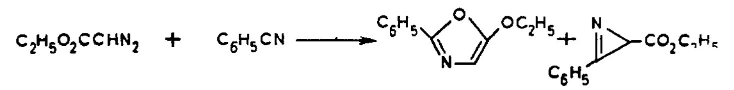
According to the data in [48], dimethoxycarbene reacts with aryl isocyanates and aryl isothiocyanates to give 5,5-dimethoxy-1,3-diarylhydantoins and thiohydantoins, respectively (in 30-50% yields).



Indolenines are formed in the reaction of methyl-substituted phenyl isonitriles with dihalocarbenes, apparently as a result of α addition of the carbene to the isonitrile and subsequent transformations of the intermediate keteneimine [49].



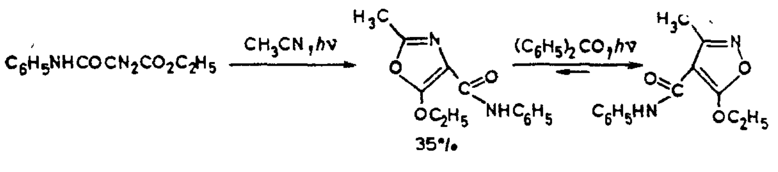
Huisgen and co-workers [50, 51] have shown that 5-ethoxy-2-phenyloxazole (30-40%) is obtained in the thermal and thermal-catalytic decomposition of diazoacetic ester in benzonitrile. According to the data in [52], the same reaction during thermolysis and photolysis leads, in addition to the oxazole, to an azirine, and in the latter case the yield reaches 5%. The formation of an oxazole can be considered to be a process involving 1,3-cycloaddition of the carbene, whereas the formation of the azirine can be considered as a process involving 1,1-cycloaddition.



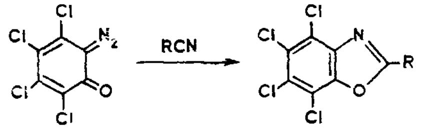
The corresponding oxazole (31%) is also obtained in the thermal-catalytic (80°, Cu) decomposition of diazoacetic ester in acetonitrile [51]. The oxazole is formed in only 3% yield during photolysis [53], whereas ethyl 2-methyl-5,5-diphenyloxazoline-4-carboxylate (9%) is obtained during irradiation in the presence of benzophenone.

It has recently been shown [54] that oxazoles are obtained in 30% yield from diazoacetic ester and acrylonitrile or methacrylonitrile in the presence of palladium acetate as the catalyst.

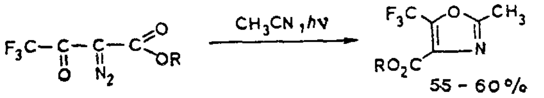
The photolysis of diazomalonanilate with light with a wavelength of 253.7 nm in acetonitrile leads to the corresponding oxazole, whereas sensitized photolysis leads to the isoxazole. It has been established that the latter is obtained from the oxazole, which is the primary reaction product [53].



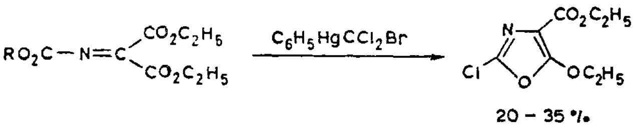
Oxazoles formed as a result of 1,3-cycloaddition of α-ketocarbenes to the C≡N bond have been obtained by thermal-catalytic or photolytic decomposition of diazoacetophenone [50], derivatives of 2-diazoindazone [55], o-quinone diazide [50, 55], and diazotrifluoroacetoacetic ester [56, 57] in nitriles.



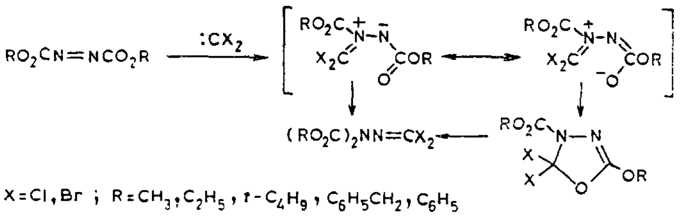
R	140°	hν
C_6H_5	36%	25%
$1\text{-}C_{10}H_7$	23%	—
CH_3	—	16%
$CO_2C_2H_5$	9%	—



Oxazole derivatives are formed as a result of formal 1,4-cycloaddition of dichlorocarbene to a conjugated system of N=C–C=O bonds [58, 59].

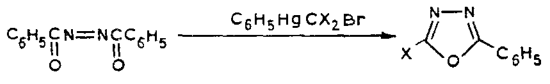


The reaction of phenyltrihalomethyl derivatives of mercury with esters of azodicarboxylic acids leads to hydrazonohalomethanes [32, 33]. A detailed study of this process showed that 1,3,4-oxadiazoline is obtained in an intermediate step. Thus the product of formal 1,4-cycloaddition of dibromocarbene – 2-methoxy-4-carbomethoxy-5,5-dibromo-Δ^2-1,3,4-oxadiazoline, which is converted by heating to the corresponding hydrazone – was isolated in 30% yield when the reaction of phenyltribromomethylmercury with dimethyl azodicarboxylate was carried out at room temperature.



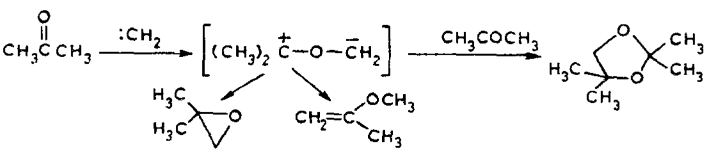
X=Cl, Br ; R=CH_3, C_2H_5, $t\text{-}C_4H_9$, $C_6H_5CH_2$, C_6H_5

In the case of azodibenzoyl, the final reaction products were 1,3,4-oxadiazoles rather than hydrazones [58, 59].

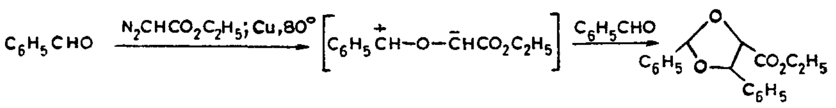


X=Cl(54%), Br(80%)

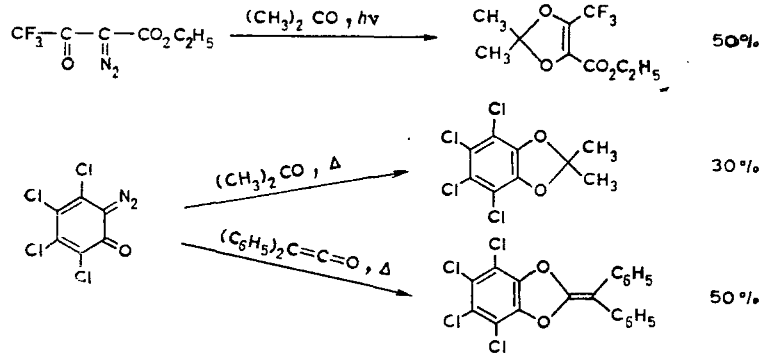
Addition to the Carbon–Oxygen Bond. 2,2-Dimethyloxirane (8%), methyl ethyl ketone (23%), and higher ketones (12%), which are products of methylene incorporation, respectively, into the C=O and C–H bonds, are obtained in the reaction of diazomethane with acetone in UV light [60, 61]. Small amounts of 2,2,4,4-tetramethyldioxolane and 2-methoxypropene, which, in the opinion of Bradley and Ledwith [61], are formed from the intermediate ylid, are simultaneously formed.



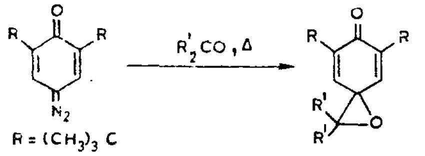
The catalytic reaction of diazoacetic ester with acetone, cyclohexanone [62], and benzaldehyde [55] does not lead to oxiranes but rather to products of conversion of the intermediate carbonyl ylid, including dioxolanes.



Trifluoroacetylcarbethoxycarbene, obtained by photolysis of the corresponding diazo compound, reacts with acetone via a 1,3-cycloaddition scheme to give a 1,3-dioxolene derivative [57, 63]. The ketocarbene formed from 3,4,5,6-tetrachlorobenzoquinone diazide behaved similarly [44].



The thermal decomposition of 2,6-di-tert-butyl-p-benzoquinone diazide leads to a carbene, which in the presence of ketones gives epoxyspiran compounds [64].

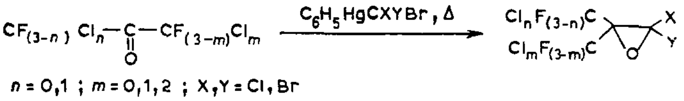


R'	R'	%
CH_3	CH_3	74
C_3H_7	C_3H_7	47
— $(CH_2)_5$ —		49

1,3-Dioxolanes [65], the formation of which evidently takes place through the intermediate methyleneoxiranes, are obtained in low yields in the reaction of fluorenylidenemethylene with acetone and some aldehydes.

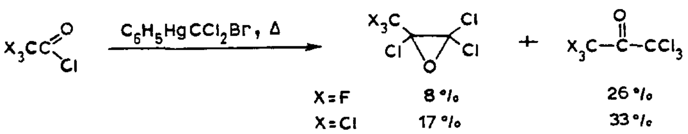
Seyferth and co-workers have studied the reaction of phenyltrihalomethyl derivatives of mercury with some carbonyl-containing compounds. It was found that phosgene, benzophenone, ethyl propyl ketone, hexachloroacetone, and sym-difluorotetrachloroacetone do not react with $PhHgCX_3$ [66].

At the same time, perhaloacetones containing more than two fluorine atoms give products of addition of dichlorocarbene to the carbonyl group (in 33-74% yields) [66, 67]. Adducts of the same ketones with chlorobromo- and dibromocarbenes, formed by heating $PhHgCClBr_2$ and $PhHgCBr_3$, respectively, are also obtained (in 25-48% yields).



sym-Tetrafluorodichloroacetone reacts with phenylfluorodibromomethylmercury at room temperature to give the corresponding gem-fluorobromooxirane (74%) [68]. Chloral and perfluorobutylaldehyde also give oxiranes on reaction with phenyldichlorobromomethylmercury. The action of the same reagent on trichloroacetyl and trifluoroacetyl chlorides leads to the formation of oxiranes and perhaloacetones [67, 69]. A more complex mixture of reaction products is obtained in the reaction of dichlorocarbene with oxalyl chloride. In the opinion of Seyferth and co-workers [67], the ketones are the products of incorporation of dichlorocarbenes at the carbon–halogen bond.

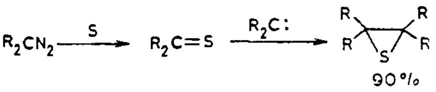
Oxiranes are obtained in the reaction of difluorocarbene, generated by pyrolysis of perfluoropropylene oxide, with fluorinated ketones [70].



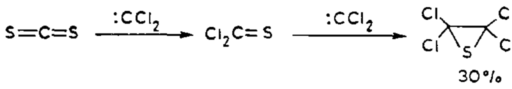
Bis(trifluoromethyl)carbene, obtained by thermal decomposition of bis(trifluoromethyl)diazirine, gives an oxirane from difluorophosgene in 40% yield [71]. The low yields of oxiranes in the reaction of carbenes with

with carbonyl compounds containing an electron-acceptor group attached to the C = O bond can be explained both by stabilization of the transition state and by an increase in the stability of the oxirane ring by the indicated groups [66].

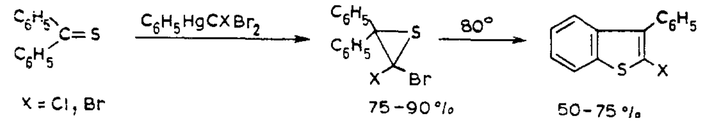
Addition to the Carbon–Sulfur Bond. Little study has been devoted to the reaction of carbenes with compounds containing a C = S bond. It has been established that thiiranes [72-75] are formed in the reaction of thioketones with diphenyldiazomethane and diazoacetic ester and that 1,3-dithiolanes [74, 75] are formed in the reaction with diazomethane. However, in the opinion of a number of investigators [72, 76-78], these reactions do not proceed through intermediate carbenes but rather through thiadiazolines. At the same time, the carbene pathway for the formation of thiiranes is proposed [79] in the reaction of diazofluorene, diazoxanthene, diazothioxanthene, and diphenyldiazomethane with sulfur or with thioketones.



Perchlorothiirane was isolated in 96% yield in the reaction of thiophosgene with phenyldichlorobromomethylmercury [80, 81]. The same thiirane is obtained in the reaction of carbon disulfide with the same reagent [34].

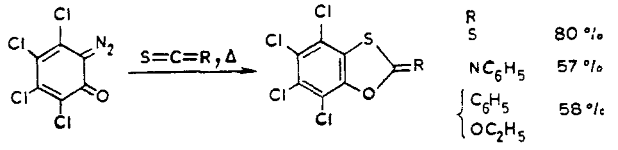


2,2-Dichloro-3,3-diphenylthiirane is obtained in 75% yield when $C_6H_5HgCCl_2Br$ is heated with thiobenzophenone [80, 81]. The same method was used to obtain thiiranes from thiobenzophenone and chlorobromo- and dibromocarbenes. Bromine-containing thiiranes are converted on heating to benzothiophene derivatives.

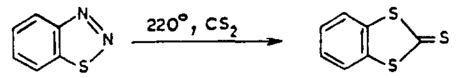


The formation of thiiranes is postulated in a number of reactions of carbenes with the C = S bond, but thiiranes are unstable under the reaction conditions and undergo subsequent transformations [38, 82, 83].

A carbene obtained from 3,4,5,6-tetrachloroquinone diazide reacts with the C = S bond of carbon disulfide and phenyl isothiocyanate via a 1,3-cyclo-addition scheme [44].



A 1,3-dithiolene derivative – the product of 1,3-cycloaddition of the thiocarbene to phenyl thioketene – is obtained in the photolysis of 4-phenyl-1,2,3-thiazole [84]. A thioketocarbene formed in the thermolysis of 1,2,3-benzothiazole reacts similarly with carbon disulfide [85].



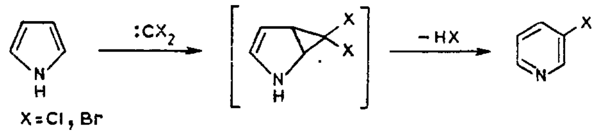
Reactions of Carbenes with the Carbon – Carbon Multiple Bond Accompanied by Opening of the Three-Carbon Ring to Give a Heteroring

Those reactions in which the carbene reacts with the C = C bond to give a heteroring as a result of the fact that a) the resulting adduct of the carbene with the C = C bond is unstable and isomerizes under the reaction conditions with opening of the cyclopropane ring and b) the carbene contains a heteroatom and is capable of reacting via a 1,3-cycloaddition scheme are analyzed in this section.

Formation of Heterocycles Containing Nitrogen, Sulfur, and Arsenic. Mono- and diadducts are obtained in the reaction of pyrrolecarboxylic acid ester with diazomethane in the presence of cuprous chloride [86]. When the monoadduct is heated to 290° it is isomerized to a dihydropyridine derivative.

Chlorocarbene generated from methylene chloride and methyllithium reacts with pyrrole, indole, skatole, and 2,3-dimethylindole to give, respectively, pyridine (32%), quinoline (13%) [87], lepidine [88], and 2,4-dimethylquinoline (6%) [89]. Similar results were obtained [90] during a study of the reaction of dibromocarbene with indole and skatole. An adduct of carbene with the C = C bond, which subsequently is rearranged with splitting out of hydrogen halide, is formed in an intermediate step in the above examples [88].

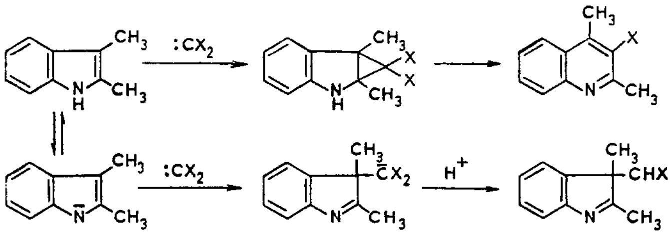
The reaction of dihalocarbenes with pyrrole and its derivatives also takes place with ring expansion to give halopyridines. 3-Halopyridines are obtained in 10-12% yields when pyrrolepotassium is heated with chloroform or bromoform [91, 92].



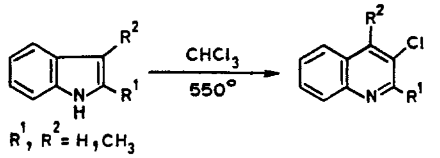
Reaction of pyrrole with dichlorocarbene in the gas phase (pyrolysis of chloroform at 550° makes it possible to raise the yield of 3-chloropyridine to 33-58% [93, 94]. From 2 to 28% 2-chloropyridine is obtained along with 3-chloropyridine [93, 94].

2,5-Dialkylpyrroles react with dichlorocarbene, generated in an alkaline medium, to give 2,5-dialkyl-2-dichloromethyl-2H-pyrroles and 2,6-dialkyl-3-chloropyridines [95, 96]. The 2H-pyrroles are not converted to pyridines under the reaction conditions, although this transformation can also be realized under the influence of butyllithium [96].

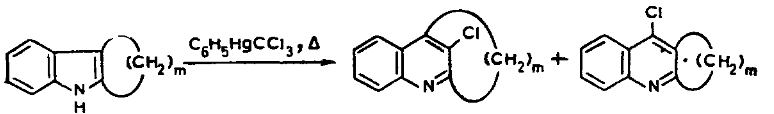
Like pyrroles, indoles are converted to 3-haloquinolines in yields of up to 10% under the conditions of the Reimer–Tiemann reaction [89, 97]. 2,3-Dimethylindole reacts with dichloro- and dibromocarbenes to give a mixture of 3-halo-2,4-dimethylquinoline and 3-dihalomethyl-2,3-dimethylindolenine, the ratio between which depends on the conditions under which the reaction is carried out [89, 98, 99]. Thus, for example, in the reaction with dichlorocarbene the quinoline/indolinine ratio changes from 0.4 for ethyl trichloroacetate and potassium tert-butoxide to 2.6 for decomposition of sodium trichloroacetate in dimethoxyethane. A similar dependence is observed for the reaction of dibromocarbene with the same indole. These data made it possible to assume that the quinoline derivative is formed as a result of the addition of the carbene to the C = C bond in the 2,3 position of the pyrrole ring with subsequent opening of the three-membered ring and that the indolenine is formed by electrophilic attack by the dihalocarbene at the 3 position in the mesomeric indolyl ion, which is present in strongly alkaline media [89, 100, 101].



The corresponding 3-chloroquinolines (in 26-42% yields) are also obtained in the reaction of indole and its methyl derivatives with dichlorocarbene in the gas phase [102].



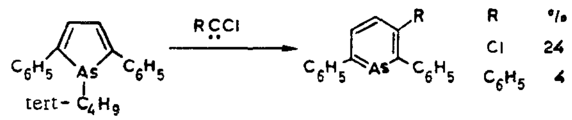
The dichlorocarbene from phenyltrichloromethylmercury reacts with 2,3-polymethyleneindoles to give 3-chloro-2,4-polymethylenequinolines and 4-chloro-2,3-polymethylenequinolines in ratios that depend on the length of the polymethylene chain [103, 104].



m = 10	70%	—
m = 8	54%	—
m = 6	49%	3%
m = 5	—	12%

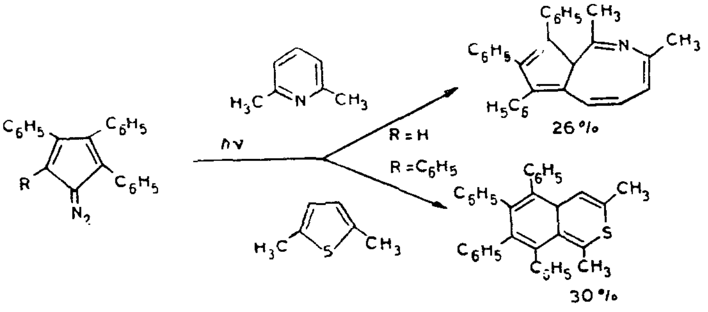
Substituted 4,4-dichloro-1-azetines are obtained by heating the products of the reaction of dichlorocarbene with unsaturated azides [105].

The reaction of 1-tert-butyl-2,5-diphenylarsacyclopentadiene with dichloro- and phenylchlorocarbenes leads to arsabenzene derivatives [106].

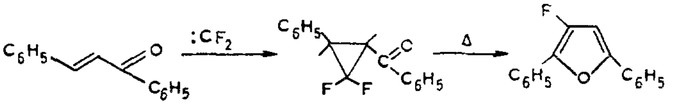


Dihydropyran reacts with chloro- and dichlorocarbenes to give adducts that are converted to 2,3-dihydrooxepine and 3-chloro-6,7-dihydrooxepine, respectively, [107] on heating with quinoline. According to the data in [108], the reaction of dichlorocarbene with benzofuran gives an adduct, the structure of which was not established; however, bis(3-chloro-3-chromene-2-yl) ether was isolated in 15% yield from the reaction mixture after treatment with water.

Photolysis of substituted diazocyclopentadienes in the presence of 2,6-lutidine or 2,5-dimethylthiophene leads to 3-azabicyclo[5.3.0]undecapentaene or 3-thiabicyclo[4.4.0]decatetraene derivatives, respectively [109], formed by 1,5-sigmatropic rearrangement of the adducts of the carbene with the C = C bonds of the starting heterocycles.

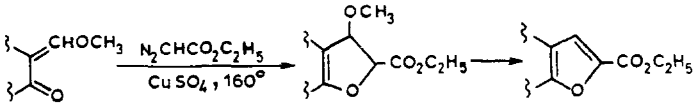


Formation of Heterocycles Containing Oxygen. 3-Fluoro-2-phenylfurans are obtained by thermal decomposition of sodium difluorochloracetate at 216° in triglyme in the presence of 2-benzylidenecyclohexanone. In the opinion of Derenberg and Hodge [110], the primary product of this reaction is cyclopropyl ketone, which at high temperature undergoes isomerization to a 2,3-dihydrofuran derivative, after which fluoride is split out. In fact, the ketone obtained from chalcone and difluorocarbene is converted to 3-fluoro-2,5-diphenylfuran (76% yield) after heating at 216° for 1.5 h.



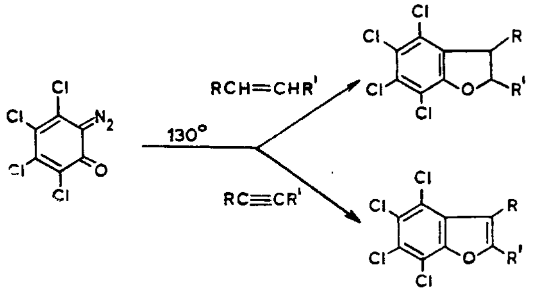
Substituted 2,3-dihydrofurans are isolated by reaction of thermally generated difluorocarbene with 2-methoxymethylene ketones [111].

Formal 1,4-cycloaddition of carbethoxycarbene to 2-methoxymethylene ketones, which leads to furan derivatives [112, 113], also takes place through 2,3-dihydrofurans, obtained by cyclization of the intermediate carbene ylid at the carbonyl oxygen atom.



According to the data in [114], a 1,3-dioxolane derivative is obtained as a result of 1,4-cycloaddition of benzocyclohexadienonylidene to 3,4,5,6-tetrachlorobenzoquinone.

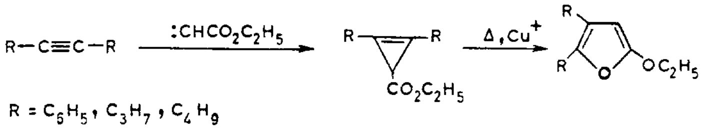
Thermal decomposition of 3,4,5,6-tetrachloroquinone diazide in the presence of unsaturated compounds leads to adducts involving 1,3-cycloaddition to the intermediate ketocarbene to the C = C bond — 2,3-dihydrobenzofuran derivatives [115]. The reaction of this carbene with acetylenes proceeds similarly [116].



R	R'	%
H	C_6H_5	21
C_6H_5	C_6H_5	18
CO_2CH_3	CO_2CH_3	57
$CO_2C_2H_5$	C_6H_5	14

R	R'	%
H	C_6H_5	39
C_6H_5	C_6H_5	28
CO_2CH_3	CO_2CH_3	48
CO_2CH_3	C_6H_5	38

The reaction of carbenes with acetylenes is widely used for the synthesis of cyclopropene derivatives. It has been established that not only cyclopropenes but also isomeric 2-alkoxyfurans are formed when the reaction of diazoacetic ester with acetylenes is carried out in the presence of copper salts used as catalysts [117]. The yields of the furans increase as the amounts of the substances used as catalysts are increased. A thorough study of this reaction shows that the furans are obtained as a result of thermal catalytic isomerization of the primary products — esters of cyclopropenecarboxylic acid [118].



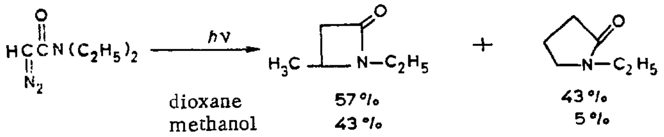
The reaction of acetyl- and benzoylcarbenes with acetylenic hydrocarbons gives the corresponding acylcyclopropenes, which also undergo thermal catalytic isomerization to furan derivatives [119].

According to the data in [120], cyclopropene derivatives are obtained by direct photolysis of dimethyl diazomalonate in the presence of acetylenes, whereas 2-alkoxy-3-methoxycarbonylfurans are produced by sensitized photolysis.

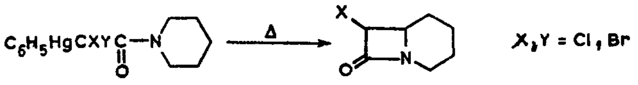
Reactions Involving Incorporation, Intramolecular Additions, and Other Transformations of Carbenes

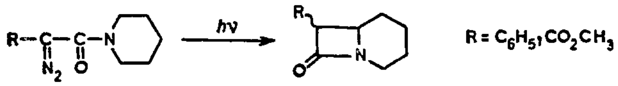
In this section processes in which carbenes are incorporated at C—H, C—N, C—O, and other bonds with the simultaneous formation of a heteroring, a change in the class of heteroring, or a change in the substituents attached to it will be analyzed.

Formation of Nitrogen-Containing Heterocycles. β-Lactams are obtained in the intramolecular incorporation of α-carbamidocarbene containing an α-CH bond at the grouping attached to the nitrogen atom. The photolysis of diazoacetic acid diethylamide leads to azetidine and pyrrolidine derivatives; the yields of the latter decrease as the dielectric permeability of the solvent increases [121]. The diallyl amide of the same acid gives both products of intramolecular incorporation at the CH bond and products of addition to the C=C bond in a ratio of 1 : 3, respectively [121].

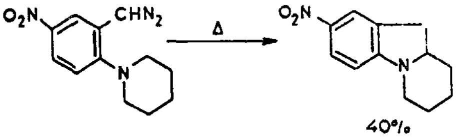


The thermolysis of organomercury compounds of the structures indicated above [122-124] or photolysis of N,N-pentamethyleneamides of phenyldiazoacetic [125, 126] and methoxycarbonyldiazoacetic [127] acids leads to carbamidocarbenes, which give 3-substituted bicyclic azetidin-2-ones in 50-60% yields; the trans configuration is preferred. The reaction has found application in the synthesis of analogs of penicillic acid [127].

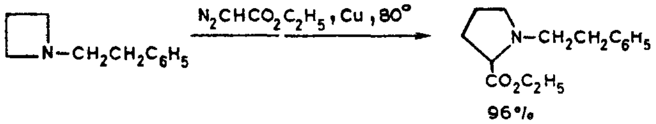




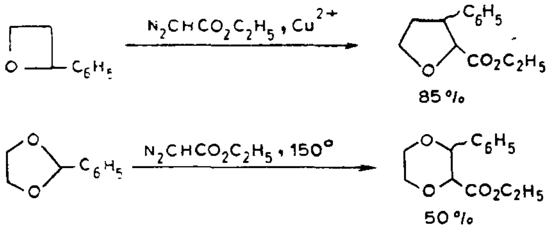
The synthesis of indoline systems is realized by intramolecular cyclization of arylcarbenes containing an o-dialkylamino group [128].



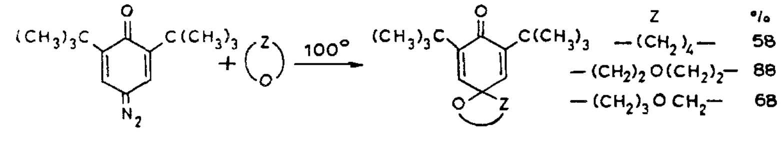
Incorporation at the C—N bond is observed in the reaction of carbethoxycarbene with N-phenylethylazetidine. N-Phenylethylpyrrolidine is inert in the same reaction, where as N-phenylethylaziridine gives ethylene and azomethine.



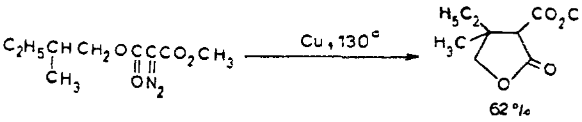
Formation of Oxygen-Containing Heterocycles. The photolysis of diazomethane or ketene with tetrahydrofuran in the gas phase leads to a mixture of various products of incorporation of methylene containing up to 20% tetrahydropyran [130]. Carbethoxycarbene is incorporated at the C—O bond of 2-phenyloxetane [131, 132], methylenedihydroxybenzene [133], and the ethyleneacetals of benzaldehyde and acetophenone [134] to give the corresponding tetrahydrofuran or 1,4-dioxane derivatives.



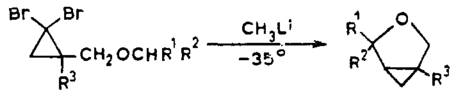
Expansion of the heteroring is also observed in the reaction of 3,5-di-tert-butylcyclohexadienonylcarbene with cyclic ethers, which, in the opinion of Nikiforov and co-workers [135], proceeds through an intermediate ylid.



The formation of 2-trimethylsilyl-3-propiolactone in the pyrolysis of methyl trimethylsilyldiazoacetate has been established [136]. Carbenes generated by thermal and photochemical decomposition of diazoacetic [137] and diazomalonic [127, 138, 139] acids give products of intramolecular incorporation — substituted α-butyrolactones. It has been established [139] that the incorporation of carbene takes place with complete retention of configuration at the reaction center.



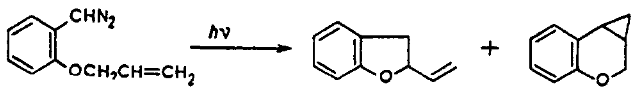
Substituted 3-oxabicyclo[3.1.0]hexanes have been synthesized [140] by incorporation of intermediate carbenes obtained from 2,2-dibromo-1-alkoxymethylcyclopropanes and methyllithium.



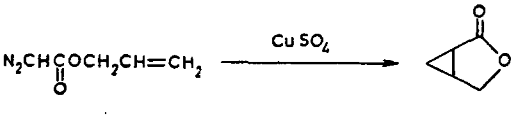
$R^1 = R^2 = R^3 = CH_3(63\%)$; $R^1 = R^2 = H$, $R^3 = CH_3(53\%)$; $R^1 = R^2 = CH_3$, $R^3 = H(61\%)$;
$R^1 = CH = CH_2$, $R^2 = R^3 = H(80\%)$

1-Methoxyisobenzofuran [141], which subsequently adds the alcohol used as the solvent, is formed in the thermal catalytic decomposition of o-methoxycarbonylphenyldiazomethane [141].

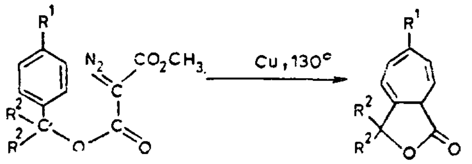
o-Allyloxyphenylcarbene from the corresponding diazo compound gives products of both intramolecular incorporation at the allyl C—H bond and addition to the C=C bond of the allyl group [142] in a ratio of 2.5 : 1.



Bicyclic and polycyclic oxygen-containing systems are obtained in 40-50% yields as a result of intramolecular cyclization of alkenyloxycarbenes [132, 143-145].

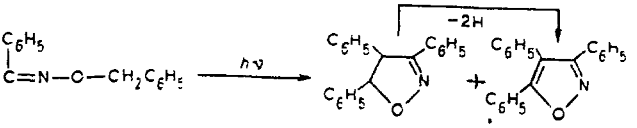


The thermal catalytic decomposition of benzyl esters of diazomalonic acid gives bicyclic lactones containing a cycloheptatriene ring [146, 147].

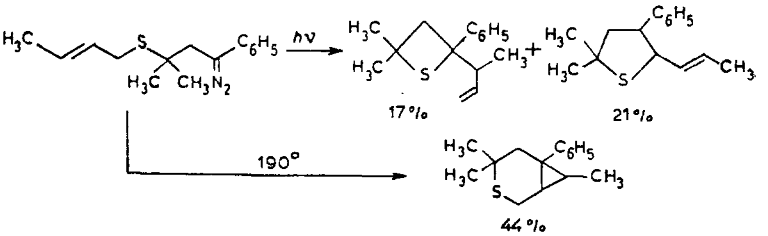


R^1	R^2	%
H	H	20
H	CH_3	45
OCH_3	H	50

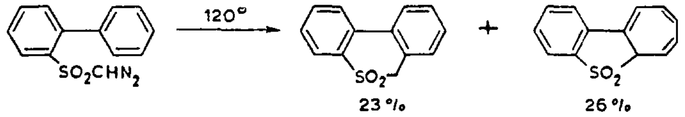
Triphenylisoxazole and small amounts of triphenylisoxazoline, which is the precursor of the isoxazole, are formed in the photolysis of 2-diazo-2-phenylacetophenone O-benzyloxime [148].



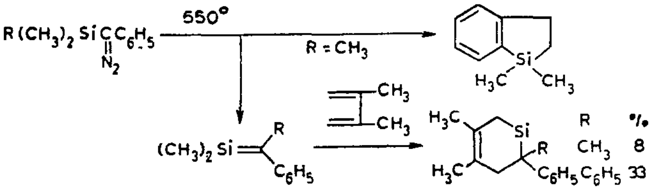
Formation of Sulfur- and Silicon-Containing Heterocycles. Products of intramolecular incorporation and rearrangement, the thermolysis of which gives products of intramolecular addition of carbene, are obtained in the photolysis of diazo compounds containing allylthiol groups [149].



The thermal decomposition of o-diazomethylsulfonyldiphenyl leads to a mixture of sulfones, formed as a result of incorporation of carbene at the C−H bond or addition to the C=C bond [150].

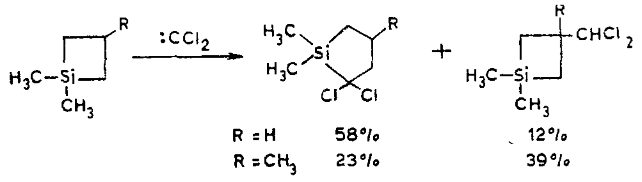


Phenyltrimethylsilylcarbene, formed from the corresponding diazo compound, is incorporated intramolecularly at the C−H bond of the phenyl group to give 1,1-dimethyl-1-silaindene [151, 152] or undergoes rearrangement to a sila olefin, which readily undergoes the diene synthesis [153].

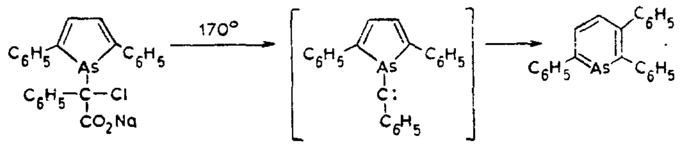


According to the data in [154], trimethylsilylcarbene, generated from the diazo compound at 440°, undergoes rearrangement to a sila olefin and is subsequently dimerized to cis- and trans-1,1,3,3-tetramethyl-1,3-disilacyclobutanes (38%).

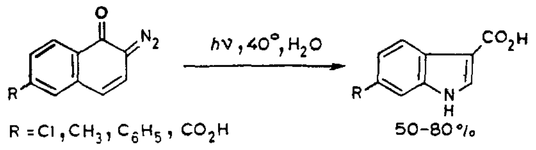
Dichlorocarbene [155-157] and carbomethoxy- and dicarbomethoxycarbenes [158] react with substituted sila- and 1,3-disilacyclobutanes to give products of incorporation at both the C−H and Si−C bonds.



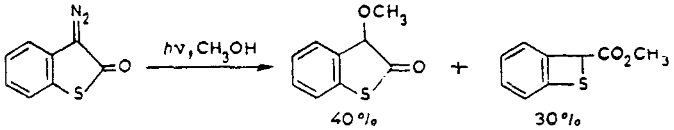
Formation of Heterocycles by Rearrangement of Carbenes. 2,3,6-Triphenylarsabenzene is obtained in 77% yield as a result of migration of the 2-C atom in the 1-arsacyclopentadienylcarbene from the arsenic atom to the carbene carbon atom [159].



Ketocarbenes formed from diazoketones are capable of undergoing diverse reactions, particularly, the Wolff rearrangement [160]. In this case, ring contraction occurs in a number of cyclic carbenes. This method has been used to synthesize pyrrole-2- and pyrrole-3-carboxylic acid and substituted indole-3- and azaindole-3-carboxylic acids [161-163].

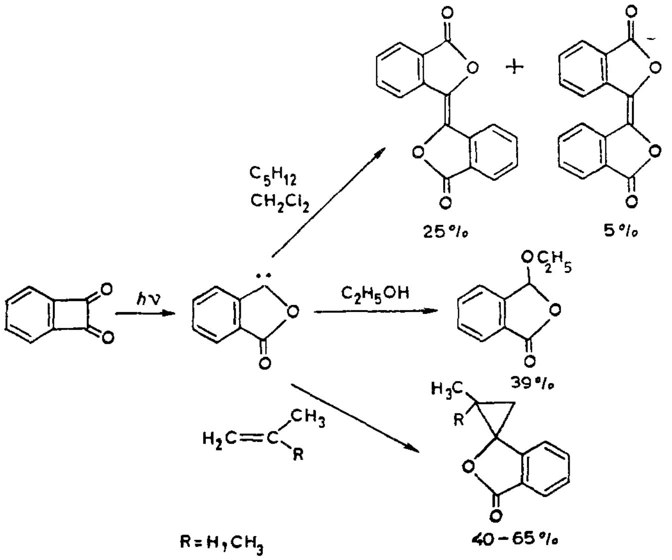


Methyl 2H-benzothiete-2-carboxylate is obtained, in addition to the corresponding methoxy derivative, in the photolysis of 3-diazo-2-oxo-2,3-dihydrobenzo[b]thiophene in methanol [164].



When the Wolff rearrangement is carried out in an aprotic medium, the resulting ketenes undergo 1,3-cycloaddition with the carbene to give methylenedioxoles [165-167] or Δ^2-butenolides [168, 169].

A study of the photolysis of cyclic ketones [170, 171], silaketones [172], and α-diketones [173, 174] showed that the corresponding hydroxycarbenes are formed in this case and are capable of undergoing addition, incorporation, and dimerization reactions. Photoisomerization occurs most readily in the case of cyclobutanones, 1,2-cyclobutanediones, and cyclopentanones with an α-cyclopropyl group. When alcohols are used as solvents, cyclic acetals are obtained. The effect of a solvent on the composition of the reaction product is evident from the data in [173] obtained in the photolysis of benzocyclobutene-1,2-dione.



The data presented in this review illustrate the great synthetic possibilities of the reactions of carbenes for the preparation of heterocyclic systems. Reactions leading to nitrogen- and oxygen-containing heterocycles have been subjected to a relatively detailed study. The investigation of methods for the synthesis of other heterocyclic systems by means of carbenes is only beginning.

The most extensive application of the carbene reaction is found in the preparation of three–six-membered heterocycles. The types of reactions of carbenes that can be used for the formation of a heteroring with a certain ring size are listed briefly below.

Three-membered heterocycles: inter- and intramolecular addition of carbenes to a carbon-heteroatom multiple bond.

Four-membered heterocycles: intramolecular incorporation of carbenes and their rearrangement.

Five-, six-, and seven-membered heterocycles: inter- and intramolecular incorporation of carbenes. 1,3- or 1,4-cycloaddition of carbenes, and isomerization or other reactions of primary adducts of carbenes with carbon—heteroatom and carbon—carbon multiple bonds.

Bicyclic, spirocyclic, and polycyclic heterocycles: inter- and intramolecular addition and incorporation of carbene.

In conclusion, it should be noted that the study of reactions of carbenes that lead to the formation of new heterocyclic systems is also of great theoretical interest for establishment of the relationship between the reactivities of organic molecules and their structures.

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