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Carbene Reactions, XX[1)]

Structural Aspects Responsible for the Thermal Extrusion of Carbenes from Norbornadienes

Reinhard W. Hoffmann[*a], *Wolfgang Barth*[a], *Reinhard Schüttler*[a], and *Bernhard Mayer*[b]

Fachbereich Chemie der Universität Marburg[a],
Hans-Meerwein-Straße, D-3550 Marburg a.d. Lahn, and

Institut für Organische Chemie der Universität Düsseldorf[b],
Universitätsstraße 1, D-4000 Düsseldorf

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The notion is put forward that norbornadienes having weak donor substituents at C-7 should suffer homolysis of the C-1/C-7 bond on heating, leading via the diradical **6** to either cycloheptatrienes or benzylic compounds. In contrast, norbornadienes having strong donor systems at C-7 should suffer heterolysis of the C-1/C-7 bond, whereupon the resulting zwitterion **7** collapses directly to carbenes in a singlet ground state.

Carben-Reaktionen, XX[1)]

Strukturelle Voraussetzungen für die Thermische Abspaltung von Carbenen aus Norbornadienen

Ein Konzept wird vorgestellt, wonach Norbornadiene mit schwachen Donor-Substituenten an C-7 beim Erhitzen eine Homolyse der C-1/C-7-Bindung erleiden. Diese führt über das Diradikal **6** zu Cycloheptatrienen oder zu Benzyl-Verbindungen. Dagegen sollen Norbornadiene, die an C-7 ausgeprägte Donor-Systeme tragen, eine Heterolyse der C-1/C-7-Bindung erleiden, worauf das so gebildete Zwitterion **7** direkt ein Carben im Singulett-Grundzustand abspaltet.

Thermolysis of norbornadienes can follow four different pathways depending on the substituents present (Scheme 1).

Path (a) results in an isomerization to benzyl-type compounds **2**. Path (b) consists in an isomerization to cycloheptatrienes **4**, probably via the norcaradienes **3**. In a third reaction mode, path (c), cleavage to benzene and a carbene **5** may ensue. Sometimes, as with norbornadiene itself[2,3,4)], all these reaction pathways occur concurrently with retro-Diels-Alder cleavage (path (d)).

Since two decades we have been interested in using reaction (c) for the generation of carbenes[5)]. During these efforts we encountered many examples of reactions (a) and (b) and necessarily started to wonder which structural features determine the thermolytic behavior of norbornadienes. The concepts which finally evolved have

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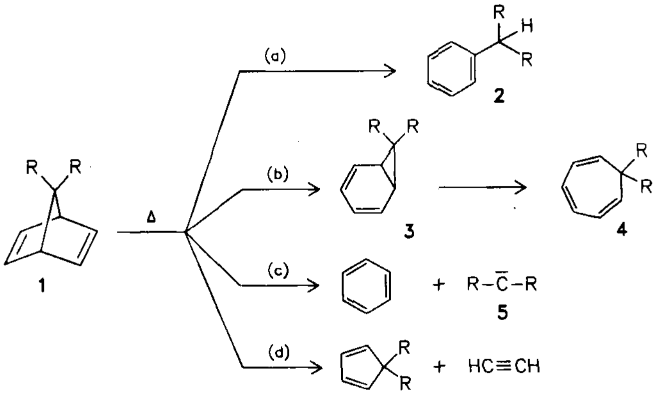
been presented in a summary[6]. Here we describe the details of the results and the full discussion.

Scheme 1

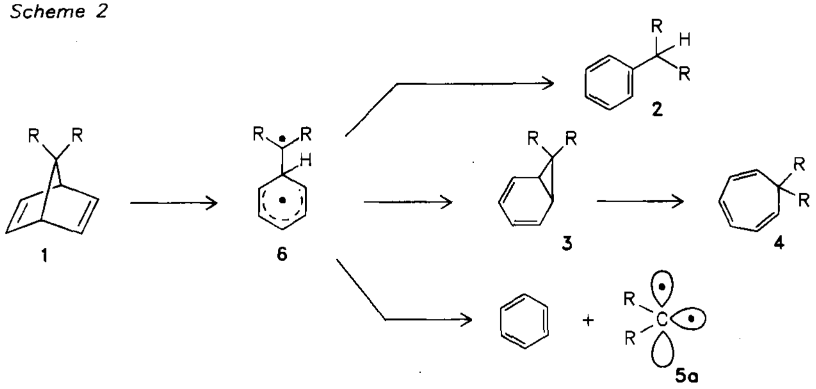


The results of our research group as well as those of others are compiled in Table 1. This table contains also data for the thermolysis of substituted quadricyclanes. These data are included because it has been found that norbornadienes, whenever tested[7–11], are the primary products of quadricyclane thermolysis. Therefore it is assumed that all the thermolysis reactions compiled in Table 1 are representative for the thermal behaviour of norbornadienes.

Mechanistic Concepts

The formation of the cycloheptatriene **4** is assumed to occur via the norcaradiene **3**. The latter could arise from **1** by a symmetry-allowed 1,3-sigmatropic shift with inversion at the migrating center. Since orbital overlap in the transition state of such a process should be exceedingly poor, formation of the norcaradiene **3** from **1** in a two-step process seems more likely. This is in line with the formation of a racemic cycloheptatriene from a chiral norbornadiene[21]. A diradical intermediate

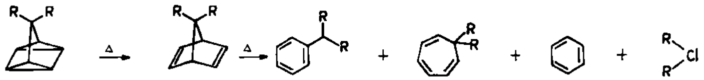
Scheme 2



6 is mostly implied[20)] for such reactions and would at the same time rationalize the formation of the benzylic products **2** as well (Scheme 2).

The cycloelimination of the bridge as a carbene could also be a synchronous cheletropic process[22)]. However, the fact that a certain process is symmetry-allowed does not imply that the synchronous pathway is for this particular reason also

Table 1. Pathways followed on thermolysis of 7,7-disubstituted norbornadienes*)



	R , R	TEMP. °C					REF.
N	CH_3O CH_3O	150			GOOD YIELD	→ $(CH_3O)_2C{=}C(OCH_3)_2$	12)
Q	$OCH_2{-}CH_2O$	FVP 200			> 95 %	→ $CO_2 + CH_2{=}CH_2$	12)
N	H N_3 **24**	FVP 410			52 %	→ $HCN + N_2$	THIS WORK, AND 13)
N	Me_3SiO N_3 **26**	FVP 250			QUANT.	→ Me_3SiNCO	THIS WORK, AND 13)
N,Q	$O{-}CH_2$	FVP 400			80 %	→ $CH_2{=}C{=}O$	11)
N,Q	$S{-}CH_2{-}CH_2{-}S$	FVP 200			75 %	→ $CS_2 + CH_2{=}CH_2$	12) 14)
Q	$S{-}(CH_2)_3{-}S$	FVP 400			84 %	→ $CS_2 + (CH_2)_3$	14)
N	$(CH)_6$	FVP 300			82 %	→ HEPTAFULVALENE	15)
Q	$(CH)_2$	FVP 250			92 %	→ SEE REF. 16)	16)
Q	NC- NMe_2	FVP 200-450			92 %	→ $NC(Me_2N)C{=}C(NMe_2)CN$	17)
Q	NC- NH_2	FVP 450			74 %	→ HCN	17)
Q	$CH_2{=}CH{-}$ NMe_2 **39**	FVP 300			65 - 85 %	→ SEE REF. 13)	THIS WORK, AND 13)
Q	$CH_3{-}\overset{O}{\overset{\Vert}{C}}{-}$ NMe_2 **34**	FVP 450			72 %	→ $Me_2N{-}CH{=}CH_2$	THIS WORK, AND 13)
N	AcO H	FVP 450	SEE REF. 18)	→ HEPTAFULVALENE (58%)			19)
N	OCN- H **30**	FVP 600	$C_6H_5CH_2NCO$ 33 %				THIS WORK, AND 13)
N	NC- H **31**	FVP 450	$C_6H_5CH_2CN$ 72 %				THIS WORK, AND 13)
Q	$O{=}S{-}CH_2{-}CH_2{-}S{=}O$	FVP 450	$C_6H_5{-}CHO$ 21 %		45 - 50 %		14)
Q	NC- $N{=}CHC_6H_5$	FVP 450	$C_6H_5CH_2{-}CN$ 9 %		49 %	→ 1-CYANOISOINDOLE	17)
Q	NC- $N{=}CH(CH_2)_2CH{=}CH_2$	FVP 400			49 %		17)
N	AcO C_6H_5	450	17 %	→ FLUORENE 74 %			8)
N	$^{\ominus}O$ H **10**	< 25		QUANT.			7)
N	Me_2N H **11**	< 10		> 80 %			17)
N	RO H	170		NEARLY QUANT.			20)
N	C_6H_5 H	170		NEARLY QUANT.			20)
N	H H	475	52 %	7 %	1 %		2)

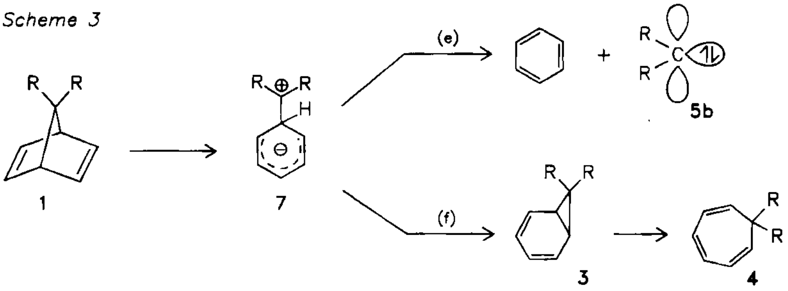
*) STARTING MATERIAL: Q: QUADRICYCLACE; N: NORBORNADIENE; FVP = FLASH VACUUM PYROLYSIS

the energetically most feasible route. A two-step process may in some cases be a better alternative[23]: Thus, there is some evidence that the cycloelimination of silylenes from sila-benzonorbornadienes related to **1** proceeds via diradicals similar to **6**[24]. It has, however, not yet been pointed out, that if the formation of carbenes from **1** were to proceed via **6**[5], the carbenes **5** would be generated with an electron occupancy shown in **5a**, i.e., the triplet or first excited singlet state!

This would be no problem for the formation of those carbenes which have triplet ground states, but inspection of Table 1 shows that the cycloeliminations observed so far led to carbenes which are either known or likely to have singlet ground states[25]. The S_0/T_1[26,27], – or S_0/S_1 – energy gap of these carbenes should probably render step **6**→**5a** (highly) endergonic. Therefore, it is questionable whether such a process could compete at all with the other stabilization reactions of the diradical **6** leading to either **2** or **3**.

Assuming that the carbenes are not generated in a one-step process from **1**, is there an intermediate that could collapse to the singlet ground state **5b** of the carbenes directly? The zwitterion **7** would be a candidate, because the electron occupancy in **7** is such that breaking of the C-1/C-7 bond would give rise directly to the singlet carbene **5b**.

Scheme 3

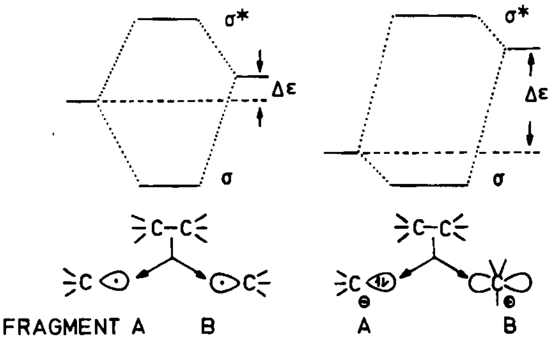


The zwitterion **7** could[20], however, also recombine to the norcaradiene **3**, eventually leading to the cycloheptatrienes **4**. This generation of **3** is another version of the two-step 1,3-sigmatropic shift, while a one-step process with retention at the migrating center would be symmetry forbidden. The outcome of a competition between the steps (e) and (f) in Scheme 3 is hard to predict, unless the stability of the carbene **5** combined with the formation of benzene render process (e) highly exothermic.

To bring this analysis to a simplified conclusion: *If the thermolysis of a norbornadiene generates a diradical* **6**, *cycloheptatriene and benzylic compounds should result. If the thermolysis leads to a zwitterion* **7**[28], *carbene generation should occur and could dominate over cycloheptatriene formation.*

According to this concept the nature of the products formed depends on whether the substituents R in **1** favor homolysis or heterolysis of the C-1/C-7 bond. How then are the electrons distributed to the fragments when a bond is being broken? If one considers the usual MO models for formation of a bond and reads them backwards the following limiting situations can be discerned[29].

Scheme 4

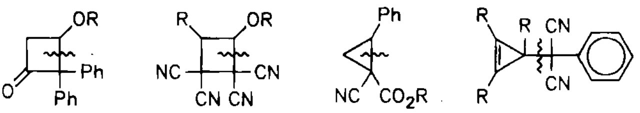


Case I: The energy of the frontier MO's in the fragments A and B are similar. After bond breaking each fragment should carry one electron, corresponding to the formation of a diradical.

Case II: The energy of the frontier MO's of the fragments differ „by a large amount", Δε. On bond breaking both electrons should go into the fragment with the lower lying MO, corresponding to bond heterolysis.

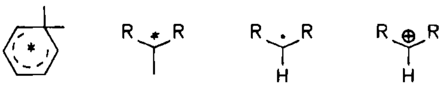
It is a moot point how large Δε must be in order to go from case I to case II. Discussion of this point with various theoreticians suggested a value for Δε in the order of 1.0 to 1.5 eV. Perhaps experimental evidence on heterolytic C—C bond cleavage may be helpful. The examples[30–34] given in Scheme 5 seem to be undisputed.

Scheme 5



From these it can be taken that the polarity difference at the ends of the bonds to be broken does not have to be huge in order to cause heterolysis[34].

Scheme 6



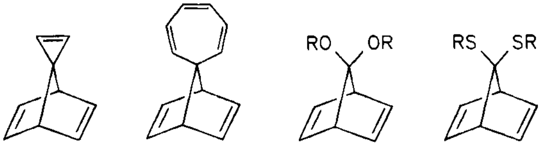
8 **9** **9a** **9b**

Returning to the bond cleavage in the norbornadiene **1**, fragment **A** is the cyclohexadienyl system **8** that remains constant for all compounds **1**. Fragment **B** is the structural element **9**. The energy of its frontier orbital should vary strongly with the nature of the substituent R. If the energy of the frontier orbital of **8** lies below that of **9**, a zwitterion of the polarity type **7** will result[28]. The energy gap between the frontier orbital of **8** and **9** can be increased by raising the energy of the frontier orbital of **9**. This is accomplished with substituents R that are π- or n-donors. i.e., all cation stabilizing substituents. This leads to the following rule: A 7,7-dialkyl-substituted norbornadiene should on thermolysis undergo homolysis, causing isomerization to **2** and **4**. With increasing donor character of the substituents at C-7 heterolysis to the zwitterion **7** should occur and should lead from a certain level of cation stabilization on to carbenes **5** and benzene. Does this concept stand the test of the facts?

Discussion

The test of this concept is not straightforward, because neither the frontier orbital energies of the intermediates **6** or **7**, nor those of the fragment model **9** are experimentally available. Inspection of the tables however supports the above concept qualitatively, because among the norbornadienes leading to carbenes are those for which the cationic center in **7** would be highly stabilized, cf. compounds in Scheme 7.

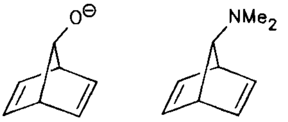
Scheme 7



Among those norbornadienes that rearrange to cycloheptatrienes **4** are those whose R substituents are less good in stabilizing carbenium ions, with the exception of **10** and **11**, which will be discussed separately. Finally, it is surprising, how many cyano-substituted norbornadienes fall into the class of the carbene generators, in as much as the cyano group is not known for its pronounced stabilization of carbenium ions[35].

To put our evaluation on a semiquantitative basis, either substituent constants or model calculations for the frontier orbital energies of the fragments **9** could be used. In the first approach, one could resort to the σ_R^+ values[36]. For those substituents for which σ_R^+ constants are available, "carbene generators" would have $\Sigma\sigma_R^+$ from -1.0 to -2.0 and "rearrangers" from 0 to -1 with two exceptions, **10**, **11**.

Scheme 8



10 11

If one feels that inductive effects on the frontier orbital energies of **6** and **7**, respectively, should not be underrated, a combination of σ_R^+ and σ_I values could be used. A parameter $\sigma_R^+ + 0.5\ \sigma_I$ is certainly arbitrary, but corresponds essentially to the m_{CXY} values[37], describing the reactivity of carbenes in olefin additions, the transition states of which are not totally unrelated to those of carbene formation by cycloelimination.

Where substituent constants are available, "carbene generators" have $\Sigma(\sigma_R^+ + 0.5\ \sigma_I)$ from -1.1 to -1.9 and "rearrangers" from 0 to -0.9, again **11** being an exception.

To test the other approach, calculations have been carried out on the model structures **9a** and **9b** for the fragment **9**. In a first evaluation the frontier orbital energies of **9a** (calculated by EHT) have been considered, cf. column 3 of Table 2. It is not the absolute values, but rather their ordering which is of significance here: Comparing these data with the thermolytic behaviour of the corresponding norbornadienes **1**, one sees that the cyano-substituted cases are the ones which fall out of order. While these estimates are very approximate, we felt that the difference in the heats of formation of the fragments **9a** and **9b** (calculated by MNDO with full geometry optimization) should better represent the trends toward homolysis or heterolysis of **1**.

Yet column 4 of Table 2 shows that there is again considerable overlap of "carbene generators", $\Delta\Delta H_f = 166-207$ kcal, and "rearrangers", $\Delta\Delta H_f = 181-224$ kcal, the picture being meddled once more by the cyano-substituted cases.

Without the latter a fairly homogenous pattern can be recognized: "carbene generators" with $\Delta\Delta H_f = 166-180$ kcal and "rearrangers" with $\Delta\Delta H_f = 178-224$ kcal.

Table 2. Calculations on the radicals **9a** and cations **9b**

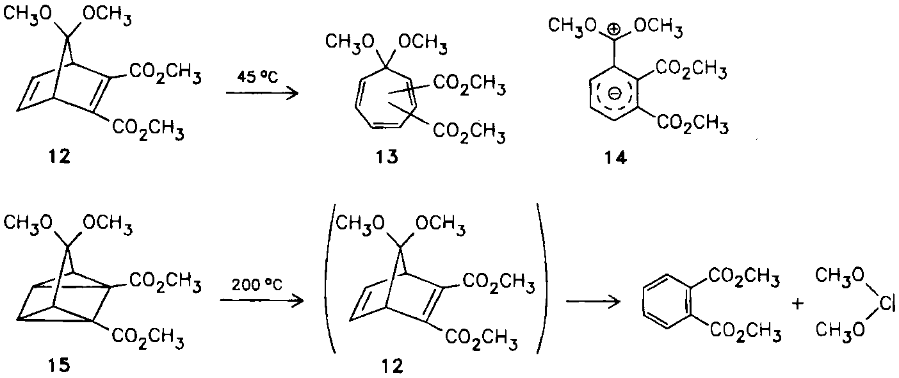
1 or 9				
R	R	HOMO of **9a** (EHT) in eV	ΔH_f **9b** − ΔH_f **9a** (MNDO) in kcal	Type of Reaction of **1**
H_3CO	OCH_3	–	165.8	Carbene
H_2N	H	–	167.4	Carbene
HO	OH	−10.0	–	–
CH=CH		–	171.0	Carbene
OCN	H	–	177.6	Rearrang.
H_3CS	SCH_3	–	180.4	Carbene
H_3CO	H	–	181	Rearrang.
HO	H	−10.66	–	(Rearrang.)
H_2N	CN	–	184	Carbene
$(H_3C)_2N$	CN	−10.72	–	Carbene
Ph	H	−10.95	186	Rearrang.
H_3CO	CN	−11.09	194	Carbene/ Rearrang.
H_3C	CH_3	−10.52	202	Rearrang.
$CH_2=N$	CN	–	207.5	Carbene
H	CN	–	224.3	Rearrang.
H	H	−11.4	–	Rearrang.

Obviously our crude model does not apply to the cyano compounds. Our model was based on the assumption (see page 3300) that the diradical **6** would not collapse to an excited singlet or triplet carbene, because this step would be too endergonic. However, cyano substituents substantially stabilize the triplet state of carbenes[27], actually rendering the X–C–CN carbenes ground state triplets[27,38]. Provided, that the intersystem crossing between a singlet and triplet diradical is rapid, it could well be that the cyano substituent stabilizes the triplet carbene to such an extent that the cleavage of **6** to benzene and a triplet carbene **5** becomes sufficiently exothermic to be the dominant reaction. This could account for the unexpected behaviour of the cyano-substituted norbornadienes, amounting to an "exceptional" formation of carbenes via the diradical **6**.

Let us now consider the "exceptional" behavior of **10** and **11**, which are expected to fragment to carbenes via the polar intermediate **7** yet form cycloheptatrienes. While strong donor substituents also favor bond homolysis[39], they should certainly accelerate heterolysis and indeed both compounds rearrange at surprisingly low temperatures. Perhaps this rearrangement represents the situation alluded to earlier, in which the cycloheptatrienes are formed via the zwitterion **7**. For that matter[7] rearrangement of **10** to the cycloheptatrienolate may be just another example of the dissociative 1,3-shift of homoallylalkoxides[40]. Since the activation energy for the step **1**→**7** is so low in the cases of **10** and **11** it may be that the reaction (f) in Scheme 3 leading to the (dimethylamino)cycloheptatriene is just more favorable than reaction (e) for entropy reasons at the low temperatures. In turn on thermolysis (>200°C) of 7-(dimethylamino)cycloheptatriene substantial amounts of benzene and (dimethylamino)carbene are generated[17,41]. It is likely that under these conditions the intermediate **7** is regenerated from the cycloheptatriene. Cleavage of **7** to benzene and the carbene ensues at the higher temperatures as in the other carbene generating thermolyses. Therefore with little additional arguments the seemingly exceptional behavior of **10** and **11** can be fitted into the concept.

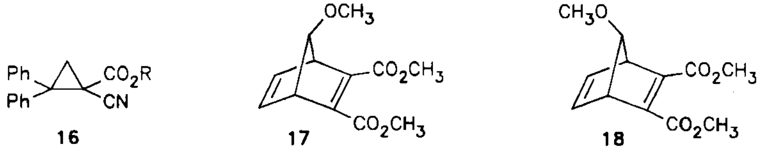
Another case where cycloheptatriene formation occurs at unusually low temperatures has been reported recently[42] (Scheme 9).

Scheme 9



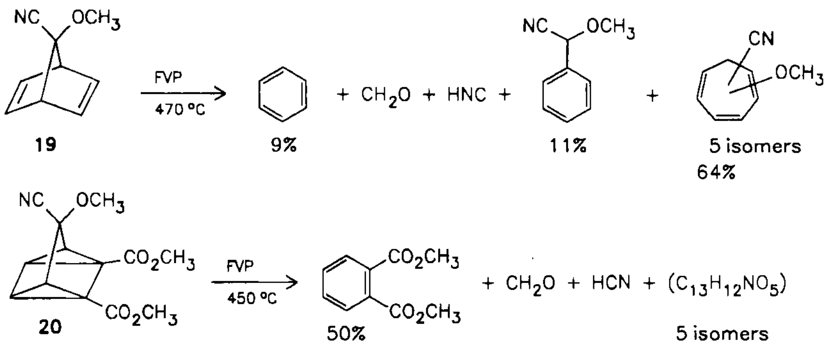
Again **12** generated at higher temperatures from **15** is cleaved to dimethyl phthalate and dimethoxycarbene[43]. This could be interpreted similarly by assuming that the zwitterion **14** is readily formed at low temperatures and collapses via the norcaradiene to a cycloheptatriene, which rearranges further. At higher temperatures the zwitterion **14** formed from the norcaradiene[14] or directly from the norbornadiene **12** ought to cleave into dimethoxycarbene and phthalate. While this is an interpretation in line with the concept presented here, *Jones*[42] argues against the intermediacy of the zwitterion **14** in the rearrangement of **12** to **13**, based on a small kinetic solvent effect of 1.2 on going from benzene to acetonitrile. It should be pointed out that large solvent effects are not necessarily observed on bond heterolysis, if the transition state lies early on the reaction coordinate and if the charges are well delocalized, as would be expected for **12**→**14**. This is demonstrated by the bond heterolysis in **16**, which showed a similarly low solvent effect of 2,3 on changing from benzene to acetonitrile at 125 °C[45]. Whatever mechanism for the rearrangement of **12** ultimately will be found to be correct, *Jones*[46] postulates a dichotomy of mechanisms to account for the ease by which **12** rearranges at 45 °C in contrast to the ethers **17** and **18** which require 160 °C. The concept presented here would allow for such a dichotomy, heterolysis for **12** and homolysis for **17** and **18**.

Scheme 10



A further corollary of the above concept is, that a shift from the homolytic pathway, Scheme 2, to the heterolytic pathway, Scheme 3, cannot only be caused by donor substituents at C-7 of **1**. Acceptor substituents at C-1 to C-6 of **1** should lower the frontier orbital of the fragment **8** and should lead to an increase in Δε. The example given in Scheme 11 might be suggestive of such an effect.

Scheme 11



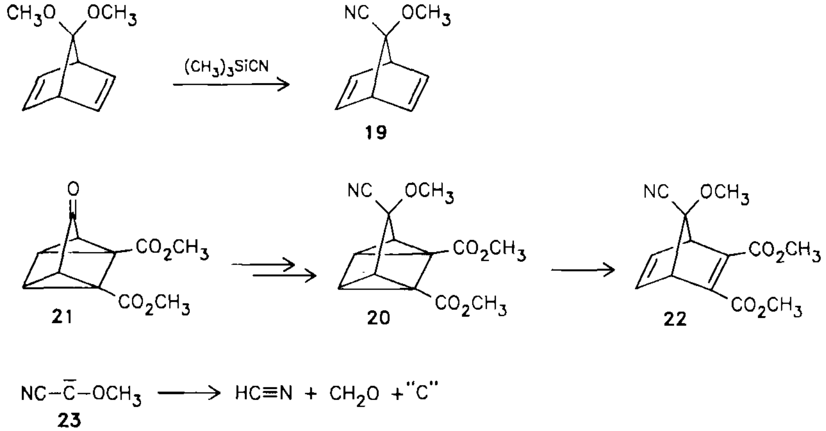
FVP = Flash Vacuum Pyrolysis

We have pointed out a new concept to rationalize the thermolytic behavior of various norbornadiene derivatives. To what extent this concept may remain valid, depends on when and what conflicting results will be discovered. This might require to abandon or to modify this concept, just as the present analysis explicitely and implicitely changes some of our earlier interpretations[5]. It may be added that the present analysis complements a study on the thermal behaviour of 7-alkylidenenorbornadienes[47], where carbene formation and retro-Diels-Alder reactions compete.

Appendix

Methoxynorbornadiene-7-carbonitrile (**19**) has been synthesized from 7,7-dimethoxynorbornadiene[12] by the action of trimethylsilyl cyanide[48].

Scheme 12



The ester-substituted derivative **20** was prepared from the quadricyclanone **21**[49]. For the assignment of its structure see reference[50]. The quadricyclane **20** was isomerized to the norbornadiene **22** by the action of norbornadiene-$PdCl_2$[51]. Thermolyses of either **20** or **22** gave identical product mixtures.

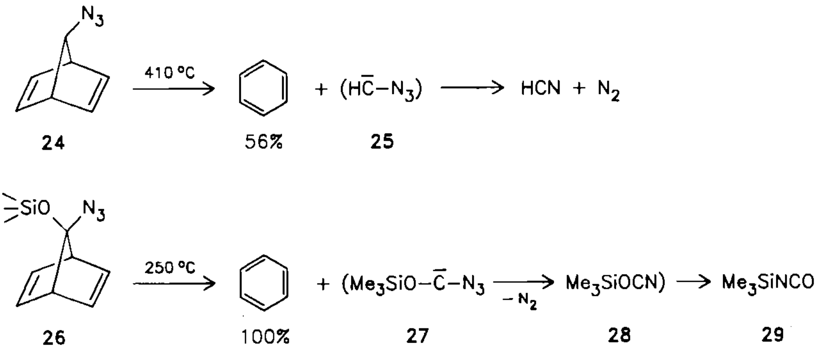
On flash vacuum pyrolysis of **19** or **20** benzene and dimethyl phthalate, respectively, were formed to some extent, indicating that the bridge had been split off presumably as the carbene **23**. However, no products directly derived from **23** have been found. Rather the formation of hydrogen cyanide and of formaldehyde suggest that the carbene **23**, if involved at all, underwent further fragmentation.

The main products of the thermolysis of **19** and of **20** were the isomeric α-methoxyphenylacetonitriles and cyanomethoxycycloheptatrienes. The structures of the latter have not rigorously been established.

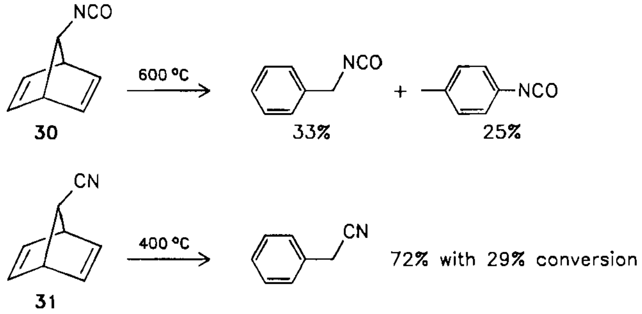
The explosive 7-azidonorbornadiene (**24**) was prepared from 7-chloronorbornadiene[52]. Its thermolysis led to benzene and hydrogen cyanide.

Similarly thermolyses of the azide **26** gave rise to benzene and trimethylsilyl isocyanate (**29**). Fragmentation of the carbenes **25** or **27** into nitrogen and a nitrile has precedent[53] as well as the easy rearrangement of the presumed trimethylsilyl cyanate (**28**) to the isocyanate **29**[54]. Flash vacuum thermolysis of the isocyanate **30**[55] and the nitrile **31**[56] required higher temperatures and resulted in isomerization to benzylic compounds. Benzene was not found in the thermolysate.

Scheme 13



Scheme 14

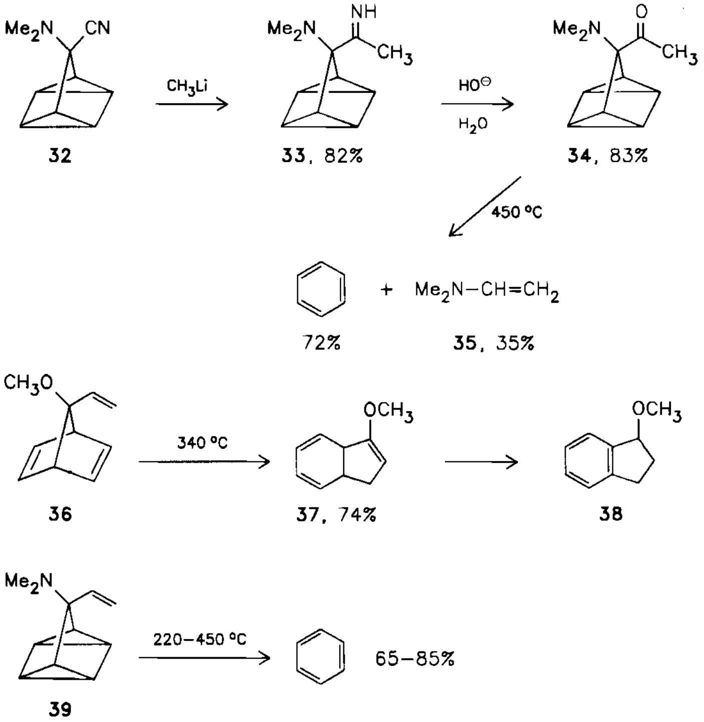


Preparation of the amino-acyl-substituted quadricyclane **34** involved addition of methyllithium to the nitrile group of **32**[17] and hydrolysis of the resulting imine **33**. Thermolysis of **34** led to benzene as the main product and a highly labile component, which could be identified by its low temperature ^1H NMR spectrum as the enamine **35**[57]. The mode of its formation, either via (dimethylamino)cyclopropanone or via (dimethylamino)methylketene and (dimethylamino)methylcarbene[58] remains obscure.

Finally, two vinyl-substituted derivatives **36** and **39** were included in this study. The former was prepared from quadricyclanone, vinylmagnesium chloride, and methyl iodide, followed by isomerization. The amino-vinyl derivative **39** resulted from the action of vinylmagnesium chloride on the nitrile **32**.

Thermolysis of **36** resulted in the Cope-rearrangement product **37**, which was highly labile towards traces of acids and isomerized readily to methoxyindane **38**[59]. Longer contact times in thermolysis resulted in a plethora of compounds; for details see ref.[13]. Benzene turned out to be the major product on thermolysis of **39**. Other products, possibly derived from (dimethylamino)vinylcarbene, have not been identified with certainty.

Scheme 15



From these results it becomes apparent that in **24**, **26**, **34**, and **39** the donor capability of the substituents at C-7 is sufficient to cause C-1/C-7 bond heterolysis on flash vacuum pyrolysis, since benzene is the major product. In the case of **36** benzene is not formed. In as much as the Cope rearrangement may be related to bond homolysis$^{60)}$ rearrangement of **36** indicates that the substituents in **36** have not enough donor character to trigger bond heterolysis. Finally, **30** and **31** clearly belong to the cases, in which isomerization to benzylic type compounds dominates.

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Experimental

All temperatures quoted are noncorrected. — ^{1}H NMR spectra: Varian T-60, Bruker WH-400. — ^{13}C NMR spectra: Bruker WH-400. — Preparative gas chromatography (GC): Aerograph A-90-P3, 1.5-m × 0.6-cm column with 5% SE 30 or QF 1 on chromosorb G, AW-DMCS (60−80 mesh), 150 ml He/min. — GC/MS: Varian MAT 711 mass spectrometer coupled to a Varian 1700 gas chromatograph with 2.5-m × 0.3-cm column with 5% SE 52 on chromosorb G (80−100 mesh), 30−250°C, 6°C/min, 40 ml N_2/min.

Syntheses

1. *7-Methoxybicyclo[2.2.1]hepta-2,5-diene-7-carbonitrile* (**19**): To a solution of 3.50 g (23.0 mmol) of 7,7-dimethoxybicyclo[2.2.1]hepta-2,5-diene[12] in 25 ml of dry CH_2Cl_2 was added 2.50 g (25.0 mmol) of trimethylsilyl cyanide. Now 0.2 ml of $BF_3 \cdot OEt_2$ was added at 0°C. After standing for 3 d at room temp. the mixture was washed three times with 20 ml each of 5% $NaHCO_3$ solution and was dried over $MgSO_4$. The solvents were removed in vacuo, and the residue was distilled at 109°C/12 Torr to give 2.4 g (69%) of **19**. – ^1H NMR ($CDCl_3$, 60 MHz): δ = 3.30 (s, 3H), 3.79 (quint. 2H), 6.52 (t, 2H), 6.72 (t, 2H).

C_9H_9NO (147.2) Calcd. C 73.45 H 6.16 N 9.52 Found C 73.36 H 6.12 N 9.56

2. *Dimethyl 3-Cyano-3-methoxytetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane-1,5-dicarboxylate* (**20**): To a solution of 3.91 g (60 mmol) of potassium cyanide in 10 ml of water was added at 0°C a solution of 11.1 g (50 mmol) of dimethyl 3-oxotetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane-1,5-dicarboxylate (**21**)[49] in 10 ml of methanol. Subsequently 7.62 g (60 mmol) of dimethyl sulfate was added dropwise. After stirring for 45 min at room temp. the precipitate was filtered and washed with few ml of methanol and of ether to give 6.96 g (53%) of **20** as colourless crystals, m.p. 111–115°C. By extraction of the aqueous mixture with ether further 0.2 g of **20** could be obtained. Recrystallization from ether yielded 4.62 g of **20**, m.p. 114–117°C. – ^1H NMR (60 MHz, $CDCl_3$): δ = 2.74 (s, 4H), 3.62 (s, 3H), 3.73 (s, 6H).

3. *Dimethyl 7-Cyano-7-methoxybicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate* (**22**): To a solution of 0.50 g (1.9 mmol) of **20** in 5 ml of CCl_4 and 1 ml of $CDCl_3$ was added 50 mg of (norbornadiene)palladium(II) chloride[51]. NMR monitoring showed that the rearrangement was complete after 10 d under reflux. After removal of the solvent in vacuo the residue was chromatographed with ether/petroleum ether (1:1) over 140 g of silica gel: 15 mg (2%) of dimethyl phthalate was followed by 350 mg (70%) of **22**, colourless crystals with m.p. 65.5–66.5 from ether/petroleum ether. – ^1H NMR (60 MHz, CCl_4): δ = 3.32 (s, 3H), 3.80 (s, 6H), 4.13 (t, 2H), 6.68 (t, 2H).

$C_{13}H_{13}NO_5$ (263.3) Calcd. C 59.31 H 4.98 N 5.32
20: Found C 59.23 H 4.95 N 5.52
22: Found C 59.42 H 4.99 N 5.41

4. *7-Azidobicyclo[2.2.1]hepta-2,5-diene* (**24**): In a solution of 3.0 g (24 mmol) of 7-chlorobicyclo[2.2.1]hepta-2,5-diene[52] in 60 ml of liquid SO_2 were suspended 5.0 g (29 mmol) of silver nitrate and 1.8 g (28 mmol) of sodium azide. The suspension was stirred for 6 h between –20 and –5°C, diluted with 20 ml of CCl_4, and filtered. Concentration of the filtrate and distillation **(bath temperature <100°C!)** resulted in 1.50 g (47%) of **24**, b.p. 41°C/1 Torr. **Caution, 24 is explosive**. – ^1H NMR (60 MHz, CCl_4): δ = 3.64 (quint, 2H), 4.64 (s, broad, 1H), 6.45 (t, 2H), 6.68 (t, 2H).

5. *7-Azido-7-(trimethylsilyloxy)bicyclo[2.2.1]hepta-2,5-diene* (**26**): A solution of 1.7 g (7.7 mmol) of 3-azido-3-(trimethylsilyloxy)tetracyclo[3.2.0.0^{2,7}.0^{4,6}] heptane[17] and of 40 mg (0.037 mmol) of $(Ph_3Sb)_2PdI_2$[61] in 5 ml of chloroform was stirred for 20 h. Distillation furnished 1.6 g (94%) of **26**, b.p. 63°C/0.1 Torr. – ^1H NMR (60 MHz, $CDCl_3$): δ = 0.18 (s, 9H), 3.67 (quint, 2H), 6.40 (t, 2H), 6.65 (t, 2H).

$C_{10}H_{15}N_3OSi$ (221.3) Calcd. C 54.27 H 6.83 N 18.98
Found C 54.09 H 6.72 N 18.58

6. *7-Isocyanatobicyclo[2.2.1]hepta-2,5-diene* (**30**): 4.1 g (27 mmol) of dry silver isocyanate was suspended in a solution of 3.00 g (23.8 mmol) of 7-chlorobicyclo[2.2.1]hepta-2,5-diene in 60 ml of dry liquid SO_2. While stirring for 6 h the solvent evaporated. The residue was

taken up in 50 ml of CCl_4. After filtration the filtrate was concentrated and distilled at 1 Torr into a receiver cooled in liquid nitrogen: 1.2 g (38%) of **30**, which has a high tendency towards polymerisation. – ^{1}H NMR (60 MHz, CCl_4): δ = 3.38 (s, 1H), 3.53 (quint, 2H), 6.6 (m, 4H).

C_8H_7NO (133.2) Calcd. C 72.16 H 5.30 N 10.52 Found C 71.99 H 5.31 N 10.15

7. *Bicyclo[2.2.1]hepta-2,5-diene-7-carbonitrile* (**31**): A solution of 170 mg (1.45 mmol) of 3-cyanotetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane[62] and of 89 mg (0.14 mmol) methyltriphenylphosphonium hexachloroantimonate in 5 ml of CH_2Cl_2 was stirred for 10 d. Preparative GC (5% SE 30, 80°C) gave 80 mg (47%) of **31** as colourless solid, m.p. 42–43°C, which is prone to hydrolysis. – ^{1}H NMR (60 MHz, $CDCl_3$): δ = 3.12 (t, 1H), 3.96 (quint, 2H), 6.77 (t, 2H), 6.86 (t, 2H).

C_8H_7N (117.2) Calcd. C 82.02 H 6.02 N 11.96 Found C 82.05 H 5.87 N 11.94

8. *3-(Dimethylamino)-3-(1-iminoethyl)tetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane* (**33**): To a solution of 2.00 g (12.5 mmol) of 3-cyano-3-(dimethylamino)tetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane (**32**)[17] in 40 ml of dry ether was added at −30°C over 15 min 7.5 ml (15 mmol) of a 2 M solution of methyllithium in ether. After stirring for 3 h the mixture was hydrolyzed with ice-water and treated for 15 min with 20 ml of a 10% aqueous NH_4Cl solution. The phases were separated, and the aqueous phase was extracted twice with 20 ml each of ether. The combined organic phases were dried over Na_2SO_4 and concentrated to give 1.8 g (82%) of **33** as tan oil. A small sample was purified by preparative GC (SE 30, 120°C). – ^{1}H NMR (60 MHz, CCl_4): δ = 1.00–1.23 (t, 2H), 1.38–1.8 (m, 4H), 1.95 (s, 3H), 2.25 (s, 6H), 9.45 (s, broad, 1H).

$C_{11}H_{16}N_2$ (176.3) Calcd. C 74.96 H 9.15 N 15.89 Found C 74.78 H 9.15 N 15.62

9. *3-(Dimethylamino)-3-(1-oxoethyl)tetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane* (**34**): A solution of 1.80 g (10.2 mmol) of **33** in 20 ml of methanol and 10 ml of 20% aqueous NaOH was heated under reflux for 5 h. After concentrating to 5 ml, 5 ml of saturated aqueous NaCl solution was added, and the mixture was extracted three times with 10 ml each of CH_2Cl_2. The combined organic phases were dried over Na_2SO_4 and concentrated. Distillation gave 1.5 g (83%) of **34**, b.p. 63°C/0.1 Torr. A small sample was purified by preparative GC (SE 30, 150°C). – ^{1}H NMR (60 MHz, CCl_4): δ = 1.1–1.3 (t, 2H), 1.3–1.83 (m, 4H), 2.2 (s, 3H), 2.33 (s, 6H).

$C_{11}H_{15}NO$ (177.3) Calcd. C 74.54 H 8.53 N 7.90 Found C 74.34 H 8.52 N 8.05

10. *3-Methoxy-3-vinyltetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane:* A solution of 1.26 g (9.4 mmol) 3-hydroxy-3-vinyltetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane[52] in 20 ml of dry THF was treated over 4 h with 0.35 g (11.6 mmol) of sodium hydride. After addition of 14 g (99 mmol) of methyl iodide the mixture was stirred for 20 h and filtered. The filtrate was concentrated to 5 ml, taken up in 15 ml of ether and filtered again. After drying over Na_2SO_4 the solvents were removed, and the residue was distilled to give 1.00 g (72%) of a colourless liquid, b.p. 73°C/12 Torr. – ^{1}H NMR (60 MHz, CCl_4): δ = 1.00–1.85 (m, 6H), 3.26 (s, 3H), 4.92–5.47 (td, 2H), 5.75–6.22 (dd, 1H).

$C_{10}H_{12}O$ (148.2) Calcd. C 81.04 H 8.16 Found C 80.94 H 8.17

11. *7-Methoxy-7-vinylbicyclo[2.2.1]hepta-2,5-diene* (**36**): 4.5 g (30 mmol) of 3-methoxy-3-vinyltetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane and 80 mg of (norbornadiene)rhodium chloride were stirred in 40 ml of CH_2Cl_2 for 12 h. Distillation at 12 Torr resulted in 3.7 g (82%) of **36**. – ^{1}H NMR (60 MHz, $CDCl_3$): δ = 3.0 (s, 3H), 3.5 (quint, 2H), 4.88–5.40 (m, 2H), 5.65–6.15 (m, 1H), 6.45–6.70 (dt, 4H). – ^{13}C NMR ($CDCl_3$): δ = 52.7, 55.4, 115.1, 117.4, 136.9, 138.3, 140.6.

$C_{10}H_{12}O$ (148.2) Calcd. C 81.04 H 8.16 Found C 80.96 H 8.06

12. *3-(Dimethylamino)-3-vinyltetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane* (**39**): 50 ml of a 1.1 M solution of vinylmagnesium chloride in THF was added over 30 min at 0°C to a solution of 7.0 g (44 mmol) of 3-cyano-3-(dimethylamino)tetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane$^{17)}$ in 100 ml of dry THF. After 10 d the mixture was hydrolyzed by addition of 5 ml of ice-water. The mixture was filtered and the residue washed with 30 ml of CH_2Cl_2. The combined organic phases were concentrated to 20 ml and washed twice with 10 ml each of alkaline saturated aqueous NaCl solution. After drying over Na_2SO_4 the solution was concentrated and the residue distilled to give 3.5 g (50%) of **39**, b.p. 89°C/12 Torr. – ^{1}H NMR (60 MHz, CCl_4): δ = 1.1 – 1.4 (m, 2H), 1.4 – 1.93 (m, 4H), 2.46 (s, 6H), 5.1 – 5.65 (td, 2H), 6.1 – 6.6 (dd, 1H).

$C_{11}H_{15}N$ (161.3) Calcd. C 81.93 H 9.38 N 8.69 Found C 81.94 H 9.46 N 8.44

Thermolyses

13. *Thermolysis of* **19**: 500 mg (3.4 mmol) of **19** was distilled from a bath of 25°C at 10^{-3} Torr over 5 h through the thermolysis apparatus III$^{47)}$ at 350°C. The products were collected in a trap at –196°C. GC separation (SE 30, 120°C) resulted in three fractions: The first one was benzene. The second one could be identified as methoxyphenylacetonitrile$^{63)}$. The third fraction was a mixture of cyanomethoxycycloheptatrienes:

C_9H_9NO (147.2) Calcd. C 73.45 H 6.16 N 9.52 Found C 73.26 H 6.12 N 9.35

GC/MS analyses showed the presence of 5 components with almost identical mass spectra: m/z = 147, 146, 132, 116, 104, 77, 51, 39.

After a similar pyrolysis of 0.80 g (5.4 mmol) of **19** at 400°C/10^{-2} Torr the liquids were removed from the cold trap by syringe. The vapors remaining in the cold trap showed the presence of HCN (Dräger test tubes) and of formaldehyde by the fuchsine-SO_2 test. By GC (3.2-m column with 5% carbowax, 150°C) the main component of the cycloheptatrienes was separated: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.57 (d, J = 7.1 Hz, 2H), 3.67 (s, 3H), 5.38 (dt, J = 9.3 and 7.1 Hz, 1H), 5.48 (d, J = 7.3 Hz, 1H), 6.24 (d, J = 9.3 Hz, 1H), 7.10 (d, J = 7.3 Hz, 1H); consistent with a 1-X,4-Y-cycloheptatriene, X, Y = CH_3O or CN. – ^{13}C NMR ($CDCl_3$): δ = 33.0 t, 56.9 q, 97.3 d, 107.5 s, 115.5 d, 120.8 s, 126.2 d, 140.7 d, 157.5 s.

A quantitative determination of the products from a pyrolysis carried out at 470°C/0.01 Torr showed the presence of 9% of benzene, 11% of methoxyphenylacetonitrile, and of 64% of methoxycyanocycloheptatrienes.

14. *Thermolysis of* **20**: 65 mg (0.25 mmol) of **20** was distilled at 0.2 Torr from a bath of 90°C as before through a thermolysis tube at 450°C. The products were condensed in a train of cold traps. GC/MS analysis of the trap at 20°C showed the presence of 5 isomers of the starting material (M^+ m/z = 263). The cold trap at –60°C contained exclusively dimethyl phthalate (by ^{1}H-NMR). The –196°C trap contained besides polymeric material HCN and formaldehyde as shown by a Fuchsine-SO_2 test.

The yield of dimethyl phthalate was determined by ^{1}H NMR from the products of a similar thermolysis to be 45 – 56%.

15. *Static Thermolysis of* **20**: 15 mg each of **20** or **22** was heated neat for 1 h at 170°C. Taken up in CCl_4 the materials showed identical ^{1}H NMR spectra.

After heating 2.63 g (10 mmol) of **20** for 1 h under ca. 10 Torr of nitrogen in a bath of 170°C the residue was taken up in ether and the solution was decolourized by boiling with norite. Removal of the solvent gave a residue (2.14 g) which deposited 0.62 g of dimethyl 4-(cyanomethoxymethyl)phthalate of m.p. 86 – 89°C on trituration with ether. The mother liquor was chromatographed over a column of 110 g of silica gel. Elution with ether/petroleum ether (40–60°C) (1 : 1) yielded another 0.37 g of the above nitrile which was combined and recrystallized from ether: m.p. 89–90°C. – ^{1}H NMR (60 MHz, $CDCl_3$): δ = 3.81 (s, 3H), 3.86 (s, 3H), 3.94 (s, 3H), 5.87 (s, 1H), 7.12 (dd, *J* = 2.5 and 8.5 Hz, 1H), 7.54 (d, *J* = 8.5 Hz, 1H), 7.62 (d, *J* = 2.5 Hz, 1H).

$C_{13}H_{13}NO_5$ (263.3) Calcd. C 59.31 H 4.98 N 5.32 Found C 59.49 H 5.05 N 5.95

Further elution furnished 0.20 g (8%) of a 1,2,3,6-tetrasubstituted cycloheptatriene as yellow crystals, m.p. 107–108°C. – ^{1}H NMR (60 MHz, $CDCl_3$): δ = 2.93 (s, 2H), 3.80 (s, 3H), 3.83 (s, 3H), 3.94 (s, 3H), 5.73 (d, *J* = 7.5 Hz, 1H), 7.48 (d, *J* = 8.5 Hz, 1H).

$C_{13}H_{13}NO_5$ (263.3) Calcd. C 59.31 H 4.98 N 5.32 Found C 59.51 H 5.02 N 5.41

16. *Thermolysis of 7-Azidobicyclo[2.2.1]hepta-2,5-diene* (**24**): 71.9 mg (0.54 mmol) of **24** was distilled from a bath of 20°C at 0.3 Torr over 1 h through the thermolysis apparatus III[47] at 410°C. The products were collected in a cold trap at –196°C. On warming HCN evaporated from the cold trap and was identified by a Dräger test tube. The reminder of the cold trap was taken up in CCl_4. The ^{1}H NMR spectrum showed the presence of 52% of benzene.

17. *Thermolysis of 7-Azido-7-(trimethylsilyloxy)bicyclo[2.2.1]hepta-2,5-diene* (**26**): 109.8 mg (0.50 mmol) of **26** was distilled from a bath of 25°C at 10^{-2} Torr over 3 h through the thermolysis apparatus I[47] at 250°C. The products were condensed in a cold trap at –196°C and taken up in 1 ml of CCl_4. The ^{1}H NMR spectrum (δ = 7.4 (s) and 0.06 (s)) as well as the ^{13}C NMR spectrum (δ = 128.3 as well as 0.71 and 123.8) indicated the quantitative formation of benzene and of trimethylsilyl isocyanate (**29**).

18. *Thermolysis of 7-Isocyanatobicyclo[2.2.1]hepta-2,5-diene* (**30**): 1.0 g (7.0 mmol) of **30** was distilled from a bath of 25°C at 1 Torr over 5 h through the thermolysis apparatus I[47] at 600°C. The products were condensed in a cold trap at –196°C and taken up in 1 ml of CCl_4. The ^{1}H NMR spectrum (δ = 2.61 (s), 4.23 (s), 6.8–7.4 (m), and 7.15 (s)) showed the presence of benzyl isocyanate and of *p*-tolyl isocyanate in yields of 33 and 25%, respectively. The nature of the products was substantiated by comparison of their GC retention times with those of authentic materials.

19. *Thermolysis of Bicyclo[2.2.1]hepta-2,5-diene-7-carbonitrile* (**31**): 22.2 mg (0.19 mmol) of **31** was distilled from a bath of 20°C at 0.01 Torr over 1 h through the thermolysis apparatus III[47] at 400°C. The products were collected in a cold trap at –196°C and taken up in 0.7 ml of CCl_4. The ^{1}H NMR spectrum showed the presence of 71% of starting material and of 21% of phenylacetonitrile.

20. *Thermolysis of 3-(Dimethylamino)-3-(1-oxoethyl)tetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane* (**34**): 144 mg (0.81 mmol) of **34** was distilled from a bath of 25°C at 10^{-2} Torr over 5 h through the thermolysis apparatus III[47] at 450°C. The products were condensed in two cold traps at –60 and –196°C. Taken up in CCl_4, the contents of the first cold trap was shown to contain 61% of benzene. The contents of the second cold trap was taken up in 0.5 ml of $CDCl_3$. The ^{1}H NMR spectrum (400 MHz) recorded at –30°C showed the presence of traces of benzene and of 35% of ethenyldimethylamine (**35**): δ = 2.58 (s, 6H), 3.50 (d, *J* = 15.1 Hz, 1H), 3.55 (d, *J* = 8.5 Hz, 1H), 6.07 (dd, *J* = 15.1 and 8.5 Hz, 1H); cf. ref.[57].

21. *Thermolysis of 7-Methoxy-7-vinylbicyclo[2.2.1]hepta-2,5-diene* (**36**): 18.7 mg (0.126 mmol) of **36** was distilled from a bath of 25°C at 10^{-2} Torr over 1 h through the thermolysis apparatus I[47] at 340°C. The products were collected in a cold trap at –196°C and taken up in 1.0 ml of CCl_4/CD_3OD (1 : 1). The ^{1}H NMR spectrum (400 MHz) showed the presence

of 66% of 1a,3a-dihydro-3-methoxyindene (**37**). – ^{1}H NMR: δ = 2.12 (m, 1 H), 2.55 (ddd, J = 14.1, 8.7, and 2.7 Hz, 1 H), 2.96 (m, 1 H), 3.3 (m, 1 H), 3.54 (s, 3 H), 4.42 (dd, 1 H), 5.50 (m, 1 H), 5.60 (m, 3 H). – Addition of $CDCl_3$ led to a rapid change of the spectrum. On GC separation (Carbowax, 140°C) 1-methoxyindane (**38**) was collected as the major product. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.08 (m, 1 H), 2.32 (m, 1 H), 2.82 (m, 1 H), 3.07 (m, 1 H), 3.40 (s, 3 H), 4.82 (dd, J = 6.5 and 3.9 Hz, 1 H), 7.25 (m, 2 H), 7.39 (d, J = 7.1 Hz, 2 H).

For comparison *1-methoxyindane* (**38**) was prepared as follows: A solution of 2.00 g (15.2 mmol) of 1-indanone in 20 ml of dry ether was added over 15 min at 0°C to a stirred suspension of 0.28 g (7.5 mmol) of lithium aluminium hydride in 10 ml of dry ether. After stirring for 14 h the mixture was hydrolyzed carefully by addition of 1 ml of water. The mixture was dried over Na_2SO_4. The filtrate was concentrated and taken up in 20 ml of dry THF to which was added over 5 min 0.50 g (20 mmol) of sodium hydride. After stirring for 30 min 15 ml (44 mmol) of methyl iodide was added. After stirring for 1 h the mixture was filtered and the filtrate was concentrated. Distillation of the residue gave 1.63 g (72%) of **38**, b.p. 94°C/20 Torr. A small sample was purified by GC (SE 30, 90°C).

$C_{10}H_{12}O$ (148.2) Calcd. C 81.04 H 8.16 Found C 80.90 H 8.14

22. *Thermolysis of 3-(Dimethylamino)-3-vinyltetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane* (**39**): 78.5 mg (0.49 mmol) of **39** was distilled from a bath of 25°C at 10^{-1} Torr over 2 h through the thermolysis apparatus I[47] at 260°C. The products were collected in a cold trap at −196°C and taken up in CCl_4. The ^{1}H NMR spectrum showed the presence of 85% of benzene.

On similar pyrolyses of 200 mg of **39** at 450°C in the thermolysis apparatus III[47] the products were condensed at −196°C. The ^{1}H NMR spectrum (400 MHz, $CDCl_3$): δ = 7.39 (benzene), 6.28 (d, J = 17.9 Hz), 6.14 (d, J = 11.7 Hz), 5.68 (dd, J = 17.8 and 11.7 Hz), suggest the presence of acrylonitrile (ca. 13%). A FI mass spectrum of the condensate showed molecular masses at m/z = 54 (31%), 53 (100), acrylonitrile?, 59 (20) trimethylamine?; 78 (25) benzene; 83 (19). The signal m/z = 53 showed at high resolution M^+ = 53.0203, calculated for C_3H_3N, 53.0266.

CAS Registry Numbers

9a (R = HO, HO): 14840-85-8 / **9a** (R = HO, H): 2597-43-5 / **9a** (R = Me_2N, CN): 104172-86-3 / **9a** (R = Ph, H): 2154-56-5 / **9a** (R = CH_3O, CN): 85359-48-4 / **9a** (R = CH_3, CH_3): 2025-55-0 / **9a** (R = H, H): 2229-07-4 / **9a** (R = CH_3O, CH_3O): 4483-45-8 / **9a** (R = H_2N, H): 10507-29-6 / **9a** (R = OCN, H): 34370-37-1 / **9a** (R = CH_3S, CH_3S): 60144-59-4 / **9a** (R = CH_3O, H): 16520-04-0 / **9a** (R = H_2N, CN): 76100-77-1 / **9a** (R = $CH_2{=}N-$, CN): 104172-90-9 / **9a** (R = H, CN): 2932-82-3 / **9a** (R = CH=CH): 60512-06-3 / **9b** (R = CH_3O, CH_3O): 23012-07-9 / **9b** (R = H_2N, H): 54088-53-8 / **9b** (R = OCN, H): 104172-87-4 / **9b** (R = CH_3S, CH_3S): 37826-39-4 / **9b** (R = CH_3O, H): 23653-97-6 / **9b** (R = H_2N, CN): 104172-88-5 / **9b** (R = Ph, H): 6711-19-9 / **9b** (R = CH_3O, CN): 29874-63-3 / **9b** (R = CH_3, CH_3): 19252-53-0 / **9b** (R = $H_2C{=}N-$, CN): 104172-89-6 / **9b** (R = H, CN): 34430-18-7 / **9b** (R = CH=CH): 26810-74-2 / **12**: 95479-12-2 / **19**: 104172-74-9 / **20**: 104172-75-0 / **21**: 17475-51-3 / **22**: 51983-47-2 / **24**: 104172-76-1 / **26**: 104172-77-2 / **29**: 1118-02-1 / **30**: 104172-78-3 / **31**: 5597-65-9 / **32**: 86840-47-3 / **33**: 104172-81-8 / **34**: 104172-79-4 / **35**: 5763-87-1 / **36**: 104172-80-7 / **37**: 104172-85-2 / **38**: 1006-27-5 / **39**: 104172-83-0 / dimethyl 4-(cyanomethoxymethyl)phthalate: 104112-84-1 / 1,2,3,6-tetrasubstituted cycloheptatriene: 104157-70-2 / cyanomethoxycycloheptatriene: 104157-69-9 / 3-hydroxy-3-vinyltetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane: 35826-03-0 / 3-methoxy-3-vinyltetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane: 104172-82-9 / 3-cyanotetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane: 5597-68-2 / 3-azido-3-(trimethylsiloxy)tetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane: 95836-05-8 / 7-chlorobicyclo[2.2.1]hepta-2,5-diene: 1609-39-8 / vinylmagnesium chloride: 75-01-4 / benzene: 71-43-2 / methoxyphenylacetonitrile: 13031-13-5 / dimethyl phthalate: 131-11-3 / benzyl isocyanate: 3173-56-6 / *p*-tolyl isocyanate: 622-58-2 / phenylacetonitrile: 140-29-4 / 1-indanone: 83-33-0

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