

tion.²⁰ If trimethylenemethane diradical is ultimately obtained upon successive excision and pruning of a specified benzenoid hydrocarbon, then the tested benzenoid hydrocarbon is also a diradical. For example, the excised internal structures of anthanthrene, benzo[ghi]perylene, and triangulene (C₂₂H₁₂ isomers) are *s-trans*-1,3-butadiene, *s-cis*-1,3-butadiene, and trimethylenemethane diradical (Figure 2), respectively; therefore, triangulene is a diradical whereas anthanthrene and benzo[ghi]perylene are not. A graphite elementary carbon-bond-network defect was defined as one produced by excising out a pyrene structural unit from a perfect graphite-tessellated structure and inserting in one of the other 419 possible pyrene isomeric structural units.³

If the parent excised internal structure has a bay region and is 2-factorable, then the corresponding larger daughter PAH6 structure also has a bay region and is 2-factorable. Thus in Figure 9, benzo[ghi]perylene has a bay region and is 2-factorable and its corresponding C₅₂H₁₈ PAH6 structure has a bay region and is 2-factorable.^{15,20} On the same basis, all the PAH6 structures having formulas belonging to the one-isomer series in Table II have no bay regions.

Concluding Remarks

A number of formula-structure and physical/chemical correlations have been established by using the formula periodic table for benzenoid polycyclic aromatic hydrocarbons. These include the average $p\pi$ -electron density, electrophilic and oxidative chemical reactivity, isomer count, and stability as predicted by the sextet rule. Although these correlations have been illustrated for even carbon benzenoid hydrocarbons in this Account, it can be shown that the reasoning on which they are based is equally applicable to odd carbon vertex

polyhexes.²¹ Since the hexagon seems to be a fundamental structure of nature, the relationships reviewed here may well find application beyond polycyclic aromatic hydrocarbons.

Appendix: Glossary of Terms

d_s	net tree disconnections of internal graph edges (positive values) or connections (negative values—called negative disconnection)
N_c	total number of carbon atoms in a PAH
N_H	total number of hydrogen atoms in a PAH
N_{Ic}	number of internal carbon atoms in a PAH having a degree of 3
N_{Pc}	number of peripheral carbon atoms in a PAH having a degree of 3
PAH6	polycyclic aromatic hydrocarbon containing exclusively fused hexagonal rings; also referred to as benzenoid and polyhex
$ P = p = N_c$	total number of graph points
p_3	number of graph points (vertices) having a degree of 3
$ Q = q$	number of graph edges (lines or C-C bonds)
q_I	number of internal graph edges
q_p	number of peripheral graph edges
r	number of rings
τ	number of rings obtained upon deletion of all internal third degree vertices from a PAH6 σ -bond graph

(21) J. R. Dias, THEOCHEM, in press.

Thermolysis of 7-Substituted Norbornadienes. Selectivity in Bond-Breaking Processes

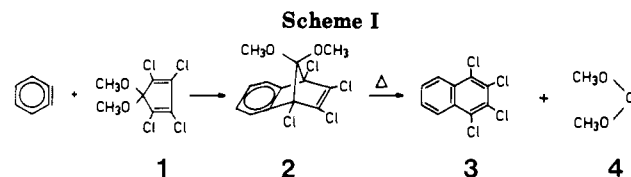
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Experiments are generally carried out with the aim of obtaining certain answers. Yet our preoccupation with science would be dull if we were to obtain only those answers for which the experiments were carried out. Excitement stems from the unexpected answers, because these often lead to new insights. In this Account I would like to present unexpected insights into the thermolytic behavior of 7-substituted norbornadienes. They would not justify their presentation,

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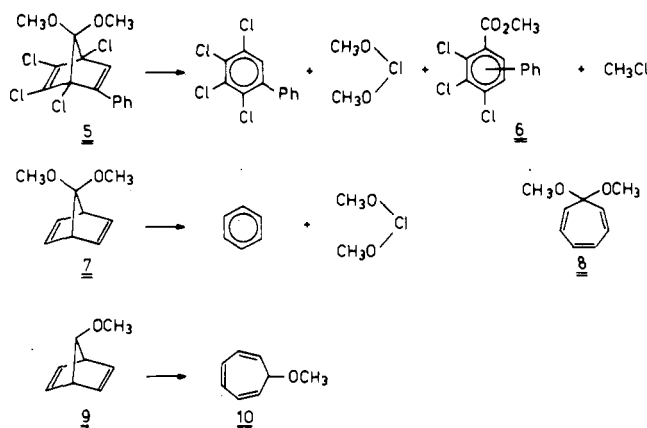


if they were not to touch on a fundamental aspect: Do we understand which bond in a given molecule or intermediate is broken on thermolysis, a question related to selectivity.

Of course, there is the classical notion of bond strength. The weakest bond breaks first.¹ Ingeniously

(1) Cf. H. M. Frey and R. Walsh, *Chem. Rev.*, **69**, 103 (1969); C. Rüdhardt, *Top. Curr. Chem.*, **88**, 1 (1980).

Scheme II

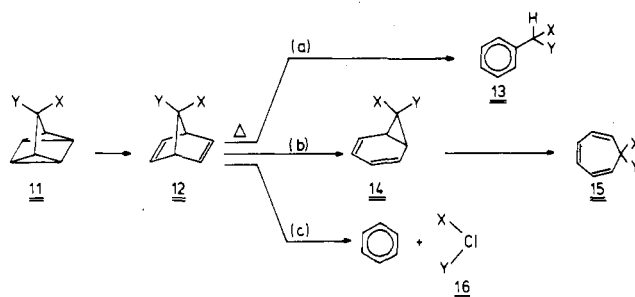


designed molecules have been studied in which increasing steric strain facilitates bond breaking.² We would like to address a more subtle phenomenon, that of substituent effects within the framework of qualitative MO considerations. This led us to a rationalization of the substituent effect in the competition between (i) carbene extrusion vs. isomerization in 7-substituted norbornadienes and (ii) carbene extrusion vs. retro-Diels–Alder cleavage in 7-alkyldenenorbornadienes.

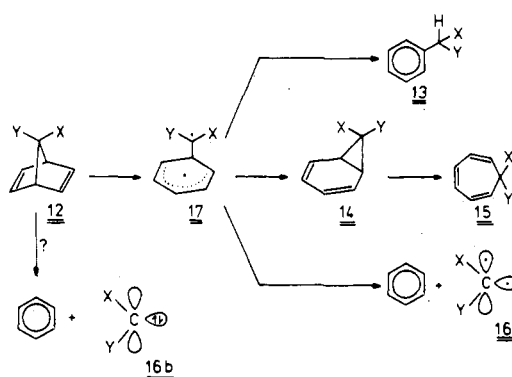
Carbene Extrusion vs. Isomerization

It all started 25 years ago with an unpublished experiment in Prof. G. Wittig's laboratory. In an attempt to trap benzyne with the diene 1, not the expected adduct 2,³ but a low yield of 3 was obtained, as a consequence of an inappropriate workup procedure: Apparently the initially formed 2 had lost dimethoxycarbene during distillation (Scheme I). Following this lead⁴ we developed a reliable method for generating dimethoxycarbene (4) using the thermolysis of 5,⁵ a reaction discovered independently by Lemal.⁶ He studied also the parent compound 7,7-dimethoxynorbornadiene (7),⁷ the thermolysis of which was much cleaner due to the lack of concurrent isomerization to 6 (Scheme II). This triggered a fruitful investigation of the reactions of dimethoxycarbene⁸ and its dimer, the electron-rich olefin tetramethoxyethylene.⁹ Nevertheless, the puzzling question remained unanswered, why thermolyses of 5 and 7 resulted in the cycloelimination of the carbene 4, while the closely related 9 cleanly isomerized to the cycloheptatriene 10.¹⁰ This question was accentuated when we found¹¹ that the

Scheme III



Scheme IV



cycloheptatriene 8 is not an intermediate in the thermolysis of 7.

Over the years a great deal of data concerning the thermolysis of 7-substituted norbornadienes 12 (and for that matter 3-substituted quadricyclanes 11) have been collected¹² which show that three sets of products may be formed: (a) isomerization to benzyne compounds 13, as in the thermolyses of norbornadiene itself;¹³ (b) rearrangement to cycloheptatrienes 15, which is assumed¹⁰ to proceed via intermediate norcaradienes 14; (c) the above-mentioned cycloelimination of carbenes (Scheme III).

Obviously, it is the nature of the substituents X and Y which determines the preferred pathway. Our interest in defining and understanding the relevant properties of the substituents extended over two decades. During this period the concept of orbital-symmetry-allowed and -forbidden reactions was developed.¹⁴ It became clear that the isomerization of a norbornadiene to a norcaradiene, 14, should not be a concerted suprafacial 1,3-shift with retention of configuration at the migrating carbon.¹⁰ Inversion is formally allowed but seemed unlikely on the grounds of insufficient orbital overlap in the transition state. Therefore, it appeared that the formation of 14 is a two-step process, involving the diradical 17, as in the thermally induced racemization of chiral norbornadiene derivatives (Scheme IV).¹⁵

The diradical 17 also accounts for the formation of the benzyne products 13. Is it also a precursor of the

(2) C. Rüdhardt and H. D. Beckhaus, *Angew. Chem.*, **92**, 417 (1980); *Angew. Chem., Int. Ed. Engl.*, **19**, 429 (1980).

(3) J. W. Wilt and E. Vasiliauskas, *J. Org. Chem.*, **35**, 2410 (1970); P. F. Ranken and M. A. Battiste, *ibid.*, **36**, 1996 (1971).

(4) Cf. related observations: E. T. McBee, W. R. Diveley, and J. E. Burch, *J. Am. Chem. Soc.*, **77**, 385 (1955); H. Feichtinger and H. Linden, *DBP* **1**, 105 862 (1961); cf. *Chem. Abstr.*, **56**, 12803 (1962).

(5) R. W. Hoffmann and H. Häuser, *Tetrahedron*, **21**, 891 (1965); R. W. Hoffmann, *Angew. Chem.*, **83**, 595 (1971); *Angew. Chem., Int. Ed. Engl.*, **10**, 529 (1971).

(6) D. M. Lemal, E. P. Gosselink, and S. D. McGregor, *J. Am. Chem. Soc.*, **88**, 582 (1966).

(7) D. M. Lemal, R. A. Lovald, and R. W. Harrington, *Tetrahedron Lett.*, 2779 (1965).

(8) W. Lilienblum and R. W. Hoffmann, *Chem. Ber.*, **110**, 3405 (1977) and previous papers in that series.

(9) R. W. Hoffmann, *Angew. Chem.*, **80**, 823 (1968); *Angew. Chem., Int. Ed. Engl.*, **7**, 754 (1968).

(10) R. K. Lustgarten and H. G. Richey, Jr., *Tetrahedron Lett.*, 4655 (1966); *J. Am. Chem. Soc.*, **96**, 6393 (1974).

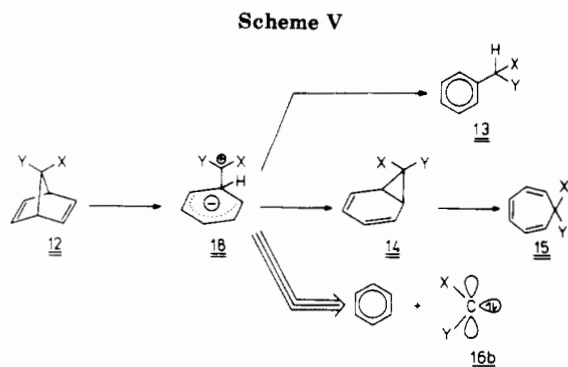
(11) R. W. Hoffmann and J. Schneider, *Tetrahedron Lett.*, 4347 (1967).

(12) R. W. Hoffmann and W. Barth, manuscript to be submitted to *Chem. Ber.*

(13) W. G. Woods, *J. Org. Chem.*, **23**, 110 (1958); W. M. Halper, G. W. Gaertner, E. W. Swift, and G. E. Pollard, *Ind. Eng. Chem.*, **50**, 110 (1958); J. H. Birely and J. P. Chesick, *J. Phys. Chem.*, **66**, 568 (1962); B. C. Roquette, *Can. J. Chem.*, **42**, 2134 (1964); W. C. Herndon and L. L. Lowry, *J. Am. Chem. Soc.*, **86**, 1922 (1964); cf. also O. Nefedow, N. Nowizkaja and A. Iwashenko, *Liebigs Ann. Chem.*, **707**, 217 (1967).

(14) R. B. Woodward and R. Hoffmann, *Angew. Chem.*, **81**, 797 (1969); *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

(15) M. R. Willcott III and C. J. Boriack, *J. Am. Chem. Soc.*, **90**, 3287 (1968); **93** 2354 (1971).



carbenes? Possibly the key to our understanding is the notion that bond breaking in 17 would lead to a carbene with an electronic configuration as shown in 16a, i.e., a triplet or excited singlet state. But typically only carbenes with singlet ground states have been liberated from norbornadienes by thermolyses.⁵ In view of the S^0/T^1 or S^0/S^1 energy differences in the carbenes, the generation of an excited state of a carbene, 16a, from 12 should be energetically unfavorable, particularly with respect to the competing isomerization to either 13 or 14.

Of course, carbenes could be formed from 12 in a symmetry-allowed synchronous cheletropic process.¹⁴ If this were the case, the observation that particularly donor substituents X and Y favor the cheletropic process relative to bond homolysis $12 \rightarrow 17$ would have to be rationalized. So far we have not found convincing arguments to support such a notion. Recently, emphasis has been placed¹⁶ on a different aspect, which we touched on from the very beginning: Just because a process involving rupture of two bonds is symmetry allowed does not necessarily mean that the stepwise alternatives are energetically less favorable. Therefore, there is no verdict that the cycloelimination of carbenes from 12 must be a concerted process!

Yet, if it is not via the biradical 17, we are left with a zwitterion, 18,^{5,6,10,17} as the intermediate. This concept has the advantage that the zwitterion 18 could collapse directly to the singlet ground state 16b of the carbene and benzene. Of course, the zwitterion 18 could also lead to the benzylic products 13 by a hydride shift or to the norcaradiene 14 via recombination. In order to explain the experimental observations, we propose the simplifying assumption that formation of benzene and the carbene is the favored pathway for the stabilization of the zwitterion 18.

This results in the heuristic concept that norbornadienes which undergo homolysis of the C-1/C-7 bond isomerize to either benzylic or cycloheptatriene derivatives, whereas those which undergo heterolysis of the C-1/C-7 bond predominantly generate benzene and a singlet carbene. The nature of the substituents X and Y determines whether homolysis or heterolysis is favored.

Where do the electrons go when a bond is being broken? If the frontier orbitals of the resulting fragments are of similar energy, the two former bonding electrons will be partitioned between the two fragments, i.e., homolytic cleavage results (Figure 1). If the energy

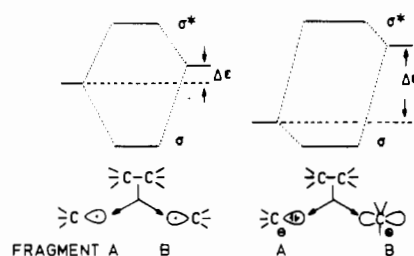


Figure 1.

difference $\Delta\epsilon$ between the two frontier orbitals of the fragments becomes sufficiently large (perhaps 1–1.5 eV), the formerly bonding electrons will stay with the fragment having the lower frontier orbital, resulting in bond heterolysis.¹⁸

Let us now apply this concept to the breaking of the C-1/C-7 bond of 7-substituted norbornadienes: This rupture creates two fragments, the cyclohexadienyl fragment (fragment A) and the moiety with the frontier orbital at C-7 (fragment B). The energy difference $\Delta\epsilon$ between these two frontier orbitals will determine whether bond homolysis or heterolysis occurs. Substituents at C-7 will not affect the energy of the frontier orbital of fragment A, the cyclohexadienyl part. Substituents will, however, strongly influence the orbital energy of fragment B and thus the energy gap $\Delta\epsilon$ between these two frontier orbitals. Provided that the frontier orbital of fragment B is energetically higher than that of fragment A, donor substituents at C-7 will raise the energy of the frontier orbital of fragment B, hence leading to an increase in $\Delta\epsilon$ and thus eventually to bond heterolysis. This is nothing other than the classical statement that cation-stabilizing substituents favor the formation of carbenium ions by bond heterolysis, including heterolysis of carbon-carbon bonds for which there are several bona fide examples.¹⁹ Those substituents at C-7 of norbornadiene that lead to carbene generation by the proposed bond heterolysis are by no means outside the range of substituents responsible for carbon-carbon bond heterolysis in the previously reported cases.¹⁹

Returning to the initial puzzle, i.e., the different thermal behavior of 7 and 9, it seems reasonable that one methoxy group is not enough to change the thermolytic pathway from homolysis leading via 17 to 10 to the heterolytic pathway leading via 18 to the carbene. Such a change might be affected by the combined action of two methoxy groups. In consequence, only those carbenes can be generated by thermolysis of norbornadienes that are structurally related to stable

(18) Cf. L. Salem and C. Rowland, *Angew. Chem., Int. Ed. Engl.*, 11, 92 (1972); *Angew. Chem.*, 84, 86 (1972).

(19) C. A. Grob, *Angew. Chem.*, 81, 543 (1969); *Angew. Chem., Int. Ed. Engl.*, 8, 535 (1969); C. Rüchardt, *Fortschr. Chem. Forsch.*, 6, 251, see p 282 (1966); R. Huisgen, L. A. Feiler, and P. Otto, *Chem. Ber.*, 102, 3405 (1969); L. A. Feiler and R. Huisgen, *ibid.*, 102, 3428 (1969); E. W. Yankee and D. J. Cram, *J. Am. Chem. Soc.*, 92, 6331 (1970); R. Huisgen and G. Steiner, *J. Am. Chem. Soc.*, 95, 5054 (1973); R. Huisgen, R. Schug, and G. Steiner, *Angew. Chem.*, 86, 47 (1974); *Angew. Chem., Int. Ed. Engl.*, 13, 80 (1974).

(20) R. W. Hoffmann, W. Barth, L. Carlson, and H. Egsgaard, *J. Chem. Soc., Perkin Trans. 2*, 1687 (1983).

(21) A. Riemann, R. W. Hoffmann, J. Spanget-Larsen, and R. Gleiter, *Chem. Ber.*, 118, 1000 (1985).

(22) H. P. Reisenauer, G. Maier, A. Riemann, and R. W. Hoffmann, *Angew. Chem.*, 96, 596 (1984); *Angew. Chem., Int. Ed. Engl.*, 23, 641 (1984).

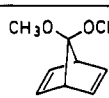



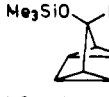
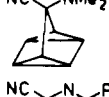
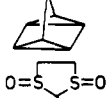
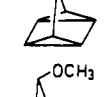
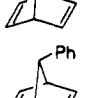
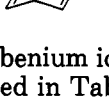
(23) W. Barth, Dissertation, Universität Marburg, 1982.

(24) R. W. Hoffmann and W. Barth, *Chem. Ber.*, 118, 634, (1985).

(16) M. J. S. Dewar, *J. Am. Chem. Soc.*, 106, 209 (1984); cf. also M. J. S. Dewar and L. Chantranupong, *J. Am. Chem. Soc.*, 105, 7161 (1983).

(17) In principle a zwitterion with reversed polarity would lead to the same conclusions.

Table I.
Selected Examples for the Thermolytic Behavior of Norbornadienes

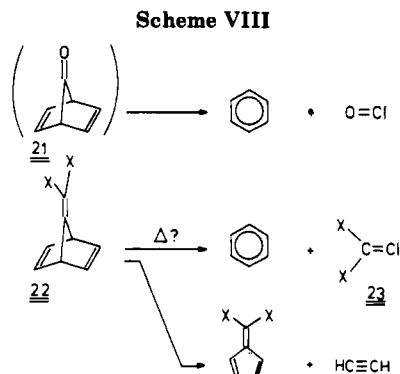
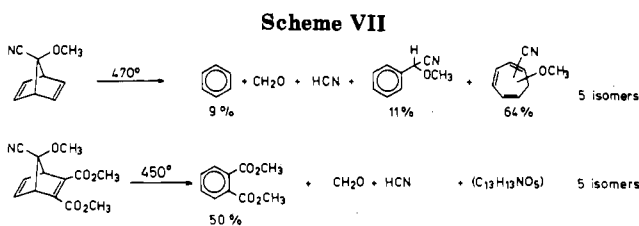
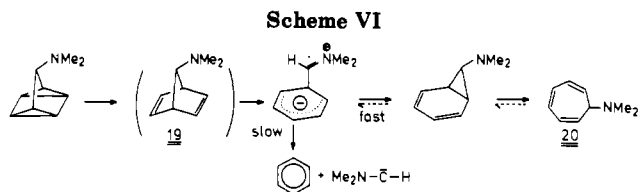
substrate	temp, °C	carbene generatn	isomerization to 13 or 15	ref
	150	+	-	7
	200	+	-	7, 20
	300	+	-	21
	250	+	-	22
	250	+	-	12, 23
	200	+	-	24
	450	+	+	24
	450	+	+	20
	170	-	+	10
	170	-	+	10

carbenium ions. This is documented by the examples listed in Table I, a more comprehensive collection of data will be published separately.¹² Connecting¹² this statement to the m_{CXY} values for carbenes of Moss,²⁵ carbene formation from norbornadienes is expected for carbenes with m_{CXY} values < -1 , as derived from $\sum(\sigma_R^+ + 0.5\sigma_I)$ for X and Y.

The situation would become boring again if all the data¹² would nicely fit into such a scheme. There are 7-cyano-substituted norbornadienes which would be expected to isomerize to cycloheptatrienes but in fact liberate carbenes²⁴ (cf. entry no. 6 of Table I). Noteworthy is also the 7-(dimethylamino)norbornadiene (19), which cleanly isomerizes to 7-(dimethylamino)cycloheptatriene (20)²⁴ at $< 10^\circ\text{C}$, instead of liberating the expected (dimethylamino)carbene. Related is the rearrangement of norbornadiene-7-olate²⁶ and of 7,7-dimethoxynorbornadiene-2,3-dicarboxylates. Certainly a 7-amino substituent in 19 should favor bond heterolysis. We believe that this is indeed the case but that at the low temperature the zwitterion 18 (Y = H; X = NMe₂) formed prefers to collapse to the norcaradiene

(25) R. A. Moss, C. B. Mallon, and C. T. Ho, *J. Am. Chem. Soc.*, **99**, 4105 (1977).

(26) B. Franzus, M. L. Scheinbaum, D. L. Waters, and H. B. Bowlin, *J. Am. Chem. Soc.*, **98**, 1241 (1976); C. Bleasdale and D. W. Jones, *Chem. Commun.* 1200 (1984).



due to entropy reasons, thus leading to the cycloheptatriene 20. This is a possibility which we had alluded to previously, but neglected in making our simplifying assumptions (Scheme VI). Yet this cycloheptatriene 20 affords benzene and products derived from the (dimethylamino)carbene²⁴ upon flash vacuum thermolysis. This result can be fitted into the general concept by postulating that at the high temperatures the zwitterion 18 is regenerated from the cycloheptatriene 20 and that carbene formation from 18 is favored in view of the positive activation entropy expected for this step.

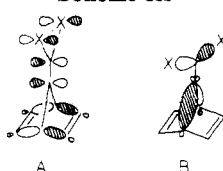
Of course, the new concept presented in this Account leads to new experiments on their own right. A switch from C-1/C-7 homolysis to C-1/C-7 heterolysis can also be anticipated if the energy of the frontier orbital of the fragment A is lowered. This can be achieved by placing electron-withdrawing substituents at C-1 to C-6 of the norbornadiene, e.g., by introducing carbomethoxy groups. There are some observations in line with such an interpretation (Scheme VII).¹² Not all the implications of this concept have been tested, nor have several old questions been answered. This applies, e.g., to the formation of 6 in the thermolysis of 5. In this case it is not clear whether 6 is formed from the zwitterion 18 or the biradical 17.^{3,5,7,10}

Carbene Extrusion vs. Retro-Diels-Alder Cleavage

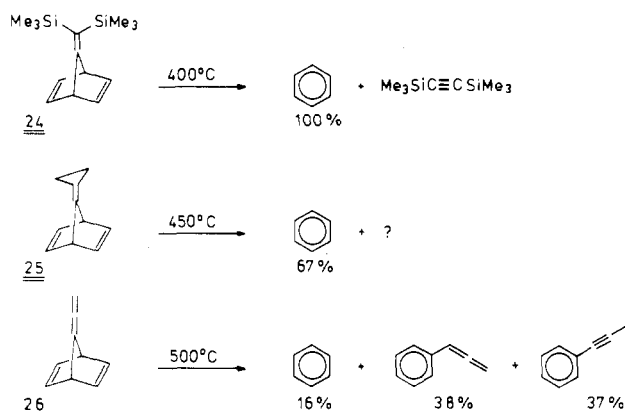
The thermal generation of carbenes from 7-substituted norbornadienes has, of course, precedent in the extremely facile decomposition of norbornadienone (21) to benzene and carbon monoxide.²⁷ An obvious ex-

(27) J. M. Landesberg and J. Siczkowski, *J. Am. Chem. Soc.*, **93**, 972 (1971). Cf. also B. F. LeBlanc and R. S. Sheridan, *Abstr. ORGN 178 of the 189th Meeting of the Am. Chem. Soc.*, 1985.

Scheme IX



Scheme X



tension would be to use an analogous cleavage reaction of 7-alkyldenenorbornadienes **22** to generate alkylidene-carbenes **23** (Scheme VIII). However, a different type of bond-breaking process presented itself in the thermolysis of 7-methylenenorbornadiene (**22**, X = H): retro-Diels-Alder cleavage led to fulvene and acetylene.^{28,29} We left the situation at that for several years, wondering what aspect of the change from oxygen to a methylene group causes the bond breaking to occur in different bond systems. The bond system A (cf. Scheme IX) is the one associated with the retro-Diels-Alder cleavage, whereas carbene formation is a reaction involving the bond system B.

It occurred to us that among several differences between **21** and **22** is the fact that norbornadienone (**21**) has lone pairs on oxygen in the bond system B. At least one lone pair would become delocalized upon breaking of the C-1/C-7 bond no matter whether this is a homolysis, heterolysis, or a concerted cheletropic process. Perhaps this delocalization could be the effect that tips the balance between the two processes (carbene elimination vs. retro-Diels-Alder cleavage) which otherwise both involve breakage of two doubly allylic bonds. To rephrase this, a high-lying occupied orbital at C-8 that can interact with the C-1/C-7/C-4 bonds of the norbornadiene should render cleavage of this bridge and hence carbene formation more facile. In order to test this idea, the compounds in Scheme X were prepared.

To bring the good news first, none of the pyrolyses of these compounds gave rise to acetylene, which indicates that retro-Diels-Alder cleavage is not taking place. Bond breaking occurred exclusively—as anticipated—in the bond system B, which was destabilized by a high-lying σ (C-Si), Walsh or π system. However, this bond cleavage proceeded cleanly only in the case of **24**. In the other cases side reactions were occurring, some of them leading to benzylic type compounds as discussed in the first section. In contrast, a number of 7-alkyldenenorbornadienes **22** with X =

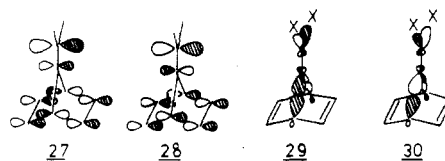


Figure 2.

CH₃, F, Br, and SR gave only retro-Diels-Alder cleavage on thermolysis.²⁹ Hence, the substituents at C-8 determine whether bond cleavage occurs in bond system A or in bond system B. The selectivity in bond breaking observed is then a consequence of varying the strength of particular bonds by the substituents. The idea is that a high-lying occupied orbital at C-8 weakens the C-1/C-7/C-4 bonds.

We then looked for some theoretical parameters of the bond strength in order to test the validity of our reasoning. Since discussion with a number of theoreticians did not reveal such a parameter, we eventually made recourse to Figure 1 in which the energy needed to break a bond is related to the energy difference between the σ and σ^* orbital defining this bond. A large σ/σ^* gap would be characteristic of strong bonds and a small gap characteristic of weak bonds. One should make a comment on using the σ/σ^* gap as a measure of bond strength rather than, e.g., the negative orbital energy of the σ orbital alone. The latter approach is complicated by inductive effects: electronegative substituents tend to lower the orbital energy of adjacent σ bonds. If judged by orbital energy alone, these bonds would therefore appear to be stronger. Yet if a similar inductive stabilization applies to the fragments resulting from breaking this bond, the inductive stabilization contributes only marginally to the bond strength in question. Inductive stabilization affects the energies of the σ and σ^* orbitals equally, which means that the inductive effect is cancelled out. Thus in comparing different systems the σ/σ^* gap should give a better approximation for the energy required to break a bond homolytically than the energy of the σ orbital alone.


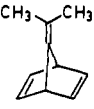

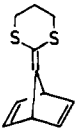
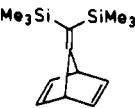



To apply these reasonings to the problem at hand—bond breaking in bond system A versus bond system B—we would need the σ/σ^* energy differences for each of these particular systems. We extracted these values from MNDO calculations on the alkyldenenorbornadienes. In doing so, one has to choose real and virtual delocalized orbitals for each bond system that have the proper symmetry relationships. Thus we presume that **27** and **28** represent σ and σ^* for the bond system A and that **29** and **30** are the representatives for bond system B (Figure 2).

The gap for the simple methylenenorbornadiene turns out to be 13.8 eV for bond system A and 16.9 eV for bond system B (Table II), in line with a preferred retro-Diels-Alder cleavage in bond system A. Changing the substituents at C-8 causes only small variations in the gap of bond system A, most cases fall between 13.4 and 13.8 eV. According to this criterion, the tendency for retro-Diels-Alder cleavage should be approximately equal in all cases studied. The σ/σ^* difference in the bond system B varies in a more pronounced manner: With nondonor substituents the values range from 16.0 to 17.9 eV, never falling in the magnitude of the values for the bond system A. Only those compounds (**24–26**) which show bond breaking in the system B due to the

(28) R. Schüttler, results from our laboratory in 1974.

(29) R. W. Hoffmann, A. Riemann, and B. Mayer, *Chem. Ber.*, **118**, 2493 (1985).

Table II.
 σ/σ^* Differences (eV) (MNDO) for Selected
 7-Alkylidenenorbornadienes

	bond system	
	A	B
	13.8	16.9
	13.5	16.6
	13.6	17.9
	13.6	16.1
	13.5	13.8
	13.7	14.7
	13.7	13.8
	16.8	13.7

donor substituents at C-8 also have low values for the σ/σ^* gap in bond system B, values around 13.8–14.6 eV: This clearly reflects the bond-weakening effect of such donor substituents.

Of course, at present the notion that the σ/σ^* gap is a useful parameter to judge the breakability of a bond remains somewhat speculative. Moreover, the σ/σ^* gap is a ground-state property, whereas the ease of bond breaking is determined by transition-state properties. We therefore accept the fact that the MNDO-derived σ/σ^* gaps of bond system B did not come out lower than those of bond system A for those compounds that

suffered bond cleavage in bond system B as a shortcoming of our model. We rather attribute significance to the strong substituent effects on the σ/σ^* gap in bond system B, a substituent effect which is in good qualitative agreement with the observed thermolytic behavior of the alkylidenenorbornadienes. In consequence, we surmise that the strength of individual bonds in complicated molecules and, hence, the selectivity in bond breaking can be estimated by comparing the σ/σ^* gaps of semilocalized orbitals from MO calculation. This could in principle aid in understanding thermolytic reactions, rearrangements of reactive intermediates, and mass spectral fragmentation processes.

It turns out that our preoccupation with the thermal generation of carbenes from norbornadienes has given us the feeling of a more general understanding of the factors which determine selectivity and polarity in bond breaking. Perhaps it is this bonus information which will be of longer lasting consequence for chemistry than the information concerning the rather special carbenes.

Conclusions

The pathways of norbornadiene thermolysis depend on the substituents at C-7: strong donor substitution favors carbene extrusion whereas in the remaining cases isomerization either to cycloheptatrienes or to benzylic compounds is observed. This varying behavior is attributed to a partitioning between heterolysis and homolysis of the C-1/C-7 bond of the norbornadienes. On thermolysis of 7-alkylidenenorbornadienes retro-Diels–Alder cleavage is generally observed. Only those compounds which have strong σ -donor substituents at C-8 result in vinylidene extrusion upon thermolysis. This changeover in pathways can be attributed to a destabilization of the C-1/C-7 bond of the 7-alkylidenenorbornadienes by the substituents at C-8. In the absence of something better we consider the σ/σ^* gap of a bond as a parameter to judge the breakability of a bond.

I am grateful to all my co-workers mentioned in the references who accumulated the information necessary to make the above-mentioned generalizations. There were "theoreticians" from all over the world with whom I discussed these concepts during the last years. I thank them for their encouragement to refine these ideas further and further. The MNDO calculations were carried out by Dr. B. Mayer of the University of Düsseldorf, to whom I am particularly obliged. Finally, all the work quoted could not have been carried out without the constant support from the Deutsch Forschungsgemeinschaft and the Fonds der Chemischen Industrie.