Carbene–Carbene Rearrangements in Solution

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We define carbene–carbene rearrangements as reactions in which an initially formed carbene rearranges to a different carbene before finally giving valence-satisfied products. These rearrangements may be conveniently subdivided into two broad categories: (1) type I rearrangements, in which the divalent carbon of the unrearranged and rearranged carbene are different; and (2) type II rearrangements, in which generation of a carbene induces molecular reorganization to give a carbene with a different structure but one in which the divalent carbon has retained its integrity.

Type I rearrangements, which in a sense resemble the more traditional rearrangements of carbonium ions, carbanions, and free radicals, include the migration of doubly bonded carbon, a reaction that is exemplified
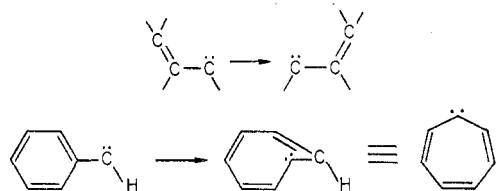
by the gas-phase rearrangement of phenylcarbene to cycloheptatrienylidene,[1,2] and migration of doubly bonded oxygen[3] or nitrogen,[3] rearrangements that are


sometimes competitive with Wolff rearrangements. Type II rearrangements are exemplified by (and, with one exception, limited to[3]) the rearrangement of vi-


nylcyclopropylidenes to cyclopentenylidenes.[3,4] This Account will discuss only type I rearrangements in which carbon is the migrating atom.

To date, type I carbene–carbene rearrangements in which carbon is the migrating atom have been limited to the interconversion of aromatic carbenes[5] (e.g., cycloheptatrienylidene, 2) and arylcarbenes[6] (e.g., phe-

nylcarbene, 1) in both the gas phase and in solution. Although this kind of interconversion was suggested as early as 1965[7] to explain unexpected products from o-methylphenylcarbene, direct evidence for the rearrangement of an arylcarbene to its aromatic counterpart did not appear until some years later. At this time it was discovered[1,2] that phenylcarbene, when generated
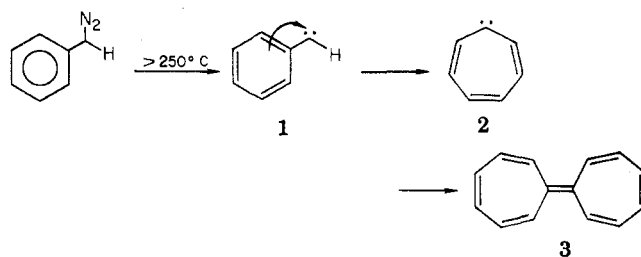
in the gas phase above 250 °C, gives the dimer of cycloheptatrienylidene, 3. That the rearrangement of phenylcarbene to cycloheptatrienylidene in the gas phase is probably reversible was demonstrated shortly thereafter when it was found that 2-phenylcyclo-heptatrienylidene (4), 2-methylcycloheptatrienylidene
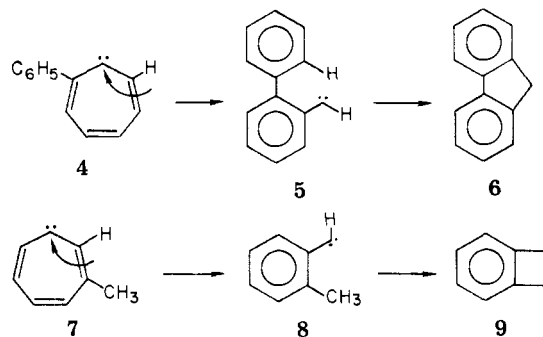
(1) R. C. Joines, A. B. Turner, and W. M. Jones, *J. Am. Chem. Soc.*, **91**, 7754 (1969).

(2) P. O. Schissel, M. E. Kent, J. J. AcAdoo, and E. Hedaya, *J. Am. Chem. Soc.*, **92**, 2147 (1970).

(3) Cf. W. M. Jones and U. Brinker in "Pericyclic Reactions", Vol. I, R. Lehr and A. Marchand, Ed., Academic Press, New York, N.Y., 1977.

(4) See L. Skattebol, *Tetrahedron Lett.*, 2361 (1970), and references cited.

(5) We define aromatic carbenes as carbenes in which the vacant orbital of the singlet state is an integral component of a Hückel aromatic system.

(6) For an excellent review see C. Wentrup, *Top. Curr. Chem.*, **62**, 173 (1976).

(7) G. G. Vander Stouw, *Diss. Abstr.*, **25**, 6974 (1975), *Chem. Abstr.*, **63**, 13126b (1965). For a complete report of this work, see G. G. Vander Stouw, A. R. Kraska, and H. Shechter, *J. Am. Chem. Soc.*, **94**, 1655 (1972).

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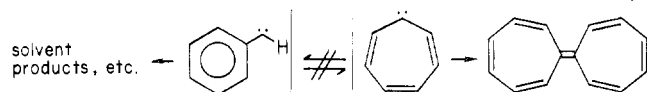
Scheme I

10

11

12

Figure 1.
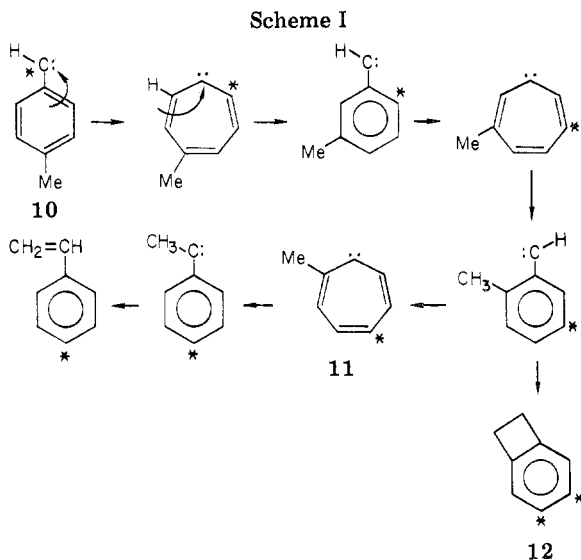
(11), and 3-methylcycloheptatrienylidene (7), when generated from their tosylhydrazone salts, give fluorene (6), styrene, and benzocyclobutene (9), respectively.[8]

Elaboration of the simple phenylcarbene–cycloheptatrienylidene interconversion has provided an attractive explanation for quite a number of otherwise unexpected gas-phase reactions of carbenes.[8-11] Of these, perhaps the most notable is the observation[11] that benzocyclobutene and styrene are formed from *p*-methylphenylcarbene (**10**). Strong support for the suggested sequence of rearrangements in Scheme I was obtained by an elegant tagged carbon study[12] in which the carbene carbon of **10** was found to reside exclusively in the indicated positions of styrene and benzocyclobutene (**12**).

In the early years of the current decade, when it was rapidly becoming clear that carbene–carbene rearrangements in the gas phase are not only real but not uncommon, it occurred to us that certain mechanistic and synthetic aspects of these rearrangements might be fruitfully probed by studying this reaction in solution. The following remarks summarize some of our efforts in this medium.

Interconversion of Aryl and Aromatic Carbenes in Solution—Introduction

Although unsubstituted phenylcarbene and cycloheptatrienylidene rapidly interconvert in the gas phase at moderate to high temperatures, this is not a typical reaction of these carbenes in solution; phenylcarbene

normally gives only products from reaction with its surroundings, and cycloheptatrienylidene—which is

much less reactive than phenylcarbene—gives only its dimer, heptafulvalene. On the other hand, over the years we have found a number of perturbed aryl and aromatic carbenes that do rearrange in solution, some under remarkably mild conditions. In an attempt to give some order to what may otherwise appear to be random observations, I shall first assume a mechanism for the rearrangement (evidence for the mechanism is given in the last section of this Account) and then consider perturbations of either the reaction conditions or the carbene structures which might be expected to facilitate reactions that go by this mechanism. The mechanism is outlined on the energy diagram[13] in Figure 1 and involves initial closure of a singlet carbene onto the π system of the aromatic ring to give a cyclopropene intermediate that then opens to the new carbene.

From the diagram in Figure 1 it is apparent that, in principle, the interconversion of aromatic and arylcarbenes should be favored by perturbations that: (a) retard the other reactions of the carbenes (dimerization of 2 or 14 or reaction of 1 with its surroundings), (b) reduce the activation energy for the rearrangement (presumably by accelerating closure to 13), or (c) shift the equilibrium between the aromatic carbene 2 and its allene 14 toward the carbene (if the fulvalene results from dimerization of the allene; vide infra). As will be seen in the following sections, carbene–carbene rearrangements in solution can, indeed, be induced by most of these perturbations.

Promotion of the Rearrangement of Aromatic Carbenes to Arylcarbenes by Retarding Dimerization

From Figure 1 rearrangement of cycloheptatrienylidene to phenylcarbene should be enhanced by either reducing the concentration of the reactive intermediate (heptafulvalene formation requires a bimolecular reaction while rearrangement is unimolecular) or retarding the dimerization. In our hands,[16] all attempts to promote the rearrangement by high dilution were unsuccessful. Elevating the thermolysis temperature (to 240 °C in tetraglyme) or varying the precursor (**16**) to the intermediate were equally ineffective. However, it was found[16] that rearrangement can be promoted by retarding the dimerization reaction. Thus, generation

(8) J. A. Myers, R. C. Joines, and W. M. Jones, *J. Am. Chem. Soc.*, **92**, 4740 (1970); W. M. Jones, R. C. Joines, J. A. Myers, T. Mitsuhashi, K. E. Krajca, E. E. Waali, T. L. Davis, and A. B. Turner, *ibid.*, **95**, 826 (1973).

(9) E.g., T. J. Barton, J. A. Kilgour, R. R. Gallucci, A. J. Rothschild, J. Slutsky, A. D. Wolf, and M. Jones, Jr., *J. Am. Chem. Soc.*, **97**, 657 (1975).

(10) C. Wentrup and K. Wilczek, *Helv. Chim. Acta*, **53**, 1459 (1970).

(11) W. J. Baron, M. Jones, Jr., and P. P. Gasper, *J. Am. Chem. Soc.*, **92**, 4739 (1970).

(12) E. Hedaya and M. E. Kent, *J. Am. Chem. Soc.*, **93**, 3283 (1971). At higher temperatures in the absence of an internal methyl trap, hydrogen rearrangements are also observed. Cf. W. D. Crow and M. N. Paddon-Row, *ibid.*, **94**, 4746 (1972); W. D. Crow and M. N. Paddon-Row, *Aust. J. Chem.*, **25**, 1705 (1973).
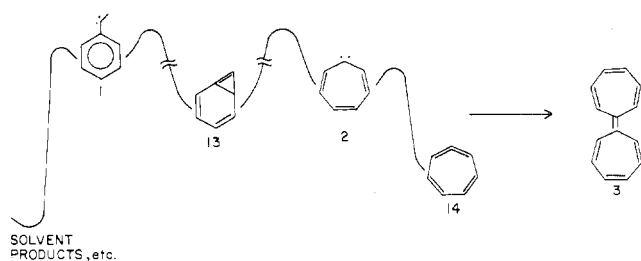
(13) Regarding the construction of this diagram, phenylcarbene is placed at higher energy than cycloheptatrienylidene which is above cycloheptatetraene on the basis of INDO calculations.[14] Other calculations[6,15] place phenylcarbene at a lower energy than cycloheptatrienylidene. The relative energy of 13 has not been calculated by any of the MO methods. However, thermochemical calculations[6] suggest that it is at an energy near the other intermediates.
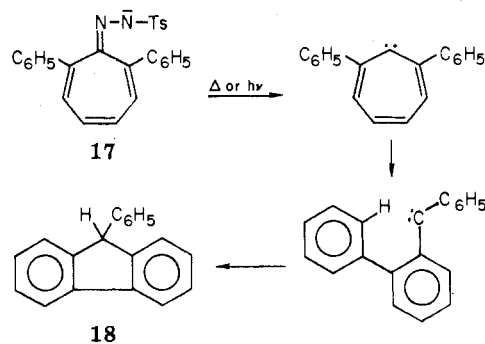
(14) R. L. Tyner, W. M. Jones, N. Y. Ohrn, and J. R. Sabin, *J. Am. Chem. Soc.*, **96**, 3765 (1974).

(15) C. Wentrup, *Tetrahedron*, **30**, 1301 (1974).

(16) Claude Mayor and W. M. Jones, unpublished results.
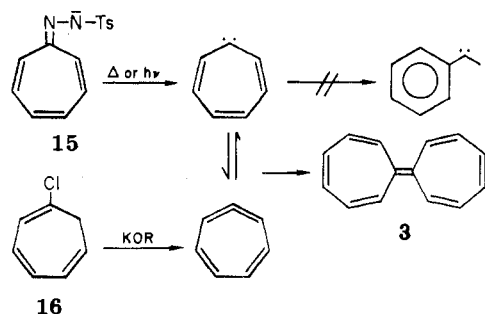
at 145 °C of 2,7-diphenylcycloheptatrienylidene from the tosylhydrazone salt 17 was found to give 62% of

9-phenylfluorene (18), the product that would be expected of a carbene–carbene rearrangement. Photolysis of 17 at 10 °C also gave 18. In similar manner, 2,7-dimethylcycloheptatrienylidene (in this case generated
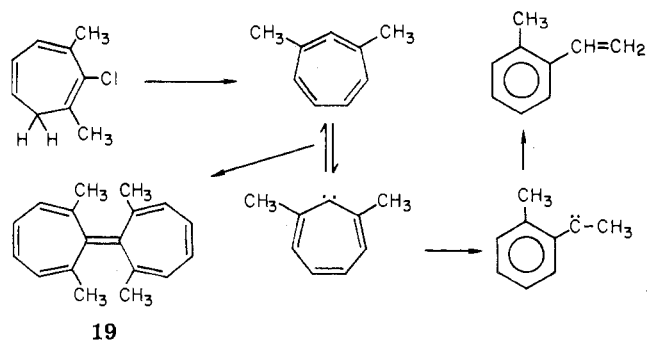

at 160 °C via the allene by dehydrochlorination of 1,3-dimethyl-2-chlorocycloheptatriene) gave about equal amounts of the tetramethylheptafulvalene 19 and o-methylstyrene, the product expected of carbene–carbene rearrangement.

Promotion of the Rearrangement of Aromatic Carbenes to Arylcarbenes by Accelerating the Ring Closure

From the energy diagram in Figure 1, a second perturbation that should favor the conversion of an aromatic carbene to its arylcarbene counterpart is one that would increase the rate of formation of the bicyclo[4.1.0]heptatriene (13). It further follows that the rate of formation of this intermediate should be facilitated by: (a) reducing the aromaticity of the rearranging carbene and in this way decreasing the loss of delocalization energy during the ring closure step and (b) shifting the allene–carbene equilibrium toward the carbene (if the dimer results from the allene).[17] Appropriately placed benzannelation of the cycloheptatrienylidene ring would be expected to do both. Thus, just as benzannelation of benzene to give naphthalene reduces the loss of aromaticity when one
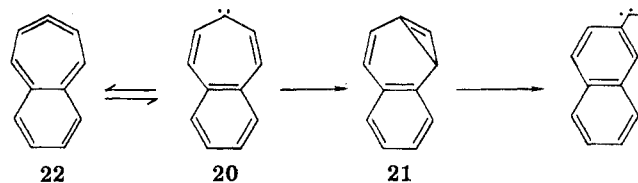
of the rings is localized, benzannelation of cycloheptatrienylidene at positions 4,5 (20)[18] or 2,3[19] should reduce the loss of aromaticity when the ring closes to the nonaromatic tricyclo[4.1.0]heptatriene 21. This essentially intuitive prediction is supported by simple Hückel calculations.[20] Benzannelation in positions 2,3 or 4,5 should also shift an equilibrium between the carbene and the allene 22 toward the carbene. This prediction is based on both resonance theory (aromaticity is destroyed in allene 22) and INDO calculations.[14] In fact, generation of 4,5-benzocycloheptatrienylidene (20) by either thermolysis (80–100
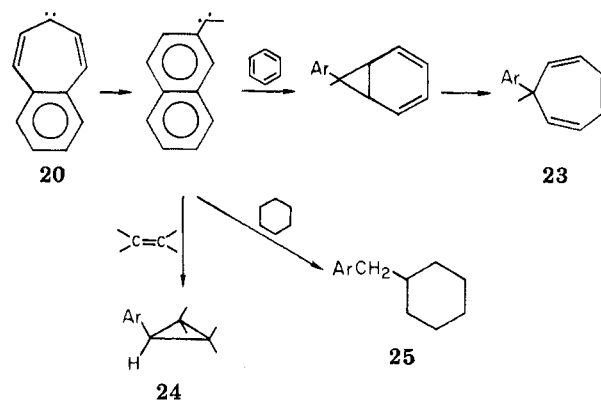
°C) or photolysis of the corresponding tropone tosylhydrazone salt (to –30 °C) gives products expected of the rearranged carbene.[18] For example, generation of 20 in benzene gives 57–97% of the expected β-naphthylcarbene addition product 23, in 2-pentene it gives the β-naphthylcyclopropanes 24, and in cyclohexane it gives the insertion product 25. In like manner, 2,3-benzocycloheptatrienylidene and 2,3:4,5-dibenzocycloheptatrienylidene give products typical of α-naphthylcarbene and 9-phenanthrylcarbene, respectively.[19,20]

Promotion of the Rearrangement of Arylcarbenes to Aromatic Carbenes by Reducing Localization Energy and Strain of the Intermediate Cyclopropene

From Figure 1 rearrangement of an arylcarbene could be enhanced by either retarding reactions with its surrounding or by increasing the rate of rearrangement. Attempts to effect rearrangement of phenylcarbene to cycloheptatrienylidene in solution by modifying the surroundings have been unsuccessful. However, modest success has been realized in our attempts to accelerate the rearrangement by perturbations that would be

(17) If heptafulvalene results from dimerization of the carbene, shifting the equilibrium toward the carbene would be counterproductive since an increase in the concentration of the carbene would have a greater accelerating effect on the bimolecular dimerization reaction than on the unimolecular rearrangement reaction. If, on the other hand, fulvalene formation originates with the allene, shifting the equilibrium toward the carbene would retard dimerization while accelerating rearrangement.
(18) K. E. Krajca, T. Mitsuhashi, and W. M. Jones, *J. Am. Chem. Soc.*, 94, 3661 (1972).
(19) P. O. Mullen and W. M. Jones, unpublished results.
(20) T. T. Coburn and W. M. Jones, *J. Am. Chem. Soc.*, 96, 5218 (1974).

Table I
Relative Localization Energies[21]

	Point of attack	Electrophilic attack		Nucleophilic attack		Radical attack	
		PPP	SPO	PPP	SPO	PPP	SPO
Benzene		0.000	0.000	0.000	0.000	0.000	0.000
Naphthalene	C-1	−0.907	−0.905	−0.915	−0.912	−0.424	−0.452
Naphthalene	C-2	−0.498	−0.539	−0.500	−0.544	−0.161	−0.248
Phenanthrene	C-9	−1.060	−1.066	−1.067	−1.081	−0.460	−0.492
1,6-Methano[10]annulene	C-2	−1.361	−1.530	−1.358	−1.525	−0.885	−1.186
1,6-Methano[10]annulene	C-4	−1.289	−1.444	−1.289	−1.444	−0.869	−1.166

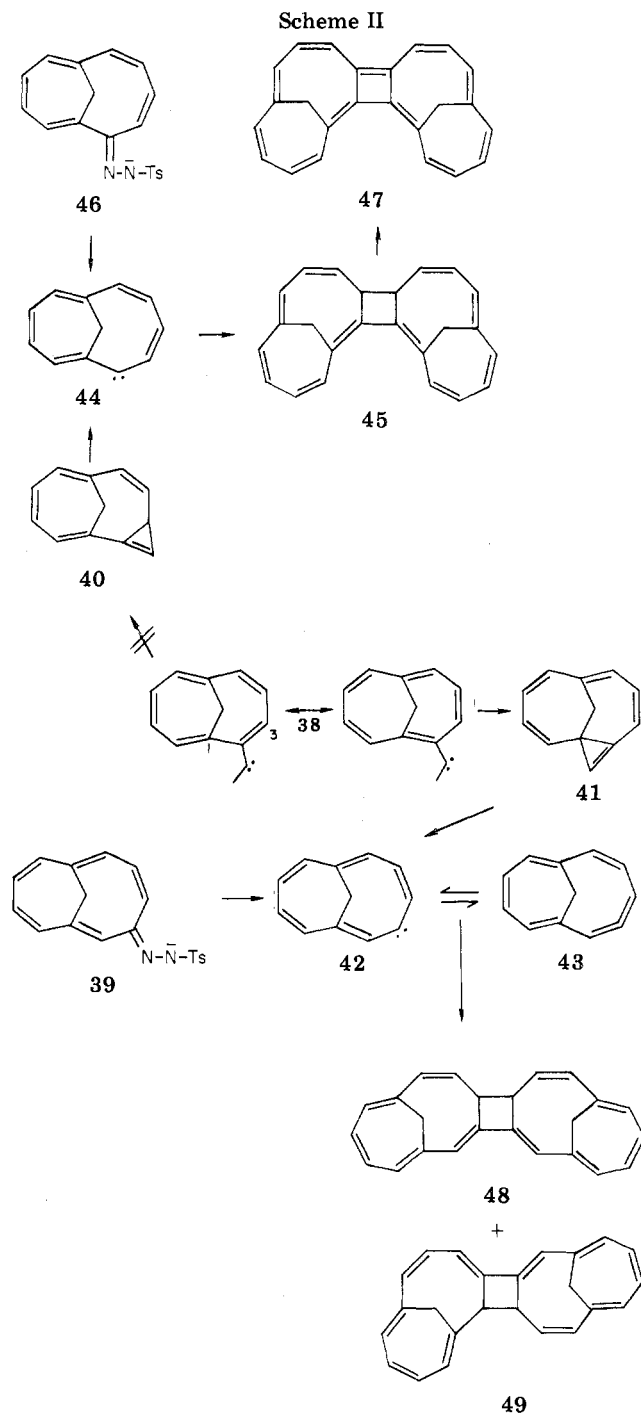expected to increase the rate of closure to the cyclopropene intermediates.

If the reactive intermediate of an aromatic substitution reaction is used as a crude model for a cyclopropene intermediate in a carbene–carbene rearrangement (for example, note that 13 is similar to 26

26   13
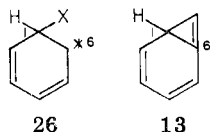
in that conjugation is interrupted at C-1 in each case and the reactive site at C-6 in 26 is replaced by a conjugated double bond in 13), the facility for rearrangement of arylcarbenes to aromatic carbenes would be expected to parallel the energies required to localize the π system of the aromatic rings. Table I lists localization energies calculated by Dewar and his group[21] for a number of aromatic systems. From these data the facility of closure should increase as the relative localization energy becomes more negative. Furthermore, models suggest that intermediates such as 32 should be somewhat less strained than bicyclo-[4.1.0]heptatrienes. Thus, arylcarbenes of 1,6-methano[10]annulene, such as 31 and 38, would be expected to undergo carbene–carbene rearrangements more rapidly than the arylcarbenes represented by the other hydrocarbons in Table I. These data also predict that if the 1,6-methanoannulenylcarbene 31 rearranges, closure at C-2 should be more facile than closure at C-4.

In the laboratory, we have found no evidence to date for carbene–carbene rearrangements (in solution) of phenyl-, naphthyl-, or phenanthrylcarbenes. However, the 10-π-electron methanoannulenylcarbene 31 does, in fact, rearrange in solution.[22] Furthermore, rearrangement goes exclusively in the direction forecast by Table I. Thus, photolysis at −45 to −50 °C of the tosylhydrazone salt 28 (synthesized in ten steps from naphthalene) gave, in addition to 35% of pyrazole 30, 41% of the same hydrocarbon that is formed from pyrolysis of the ketone tosylhydrazone salt 37.[23] No detectable quantity of the products that would be expected if closure occurred at C-4—48 and 49, which were formed from pyrolysis of the ketone tosylhydrazone salt[24] 39 (Scheme II)—were detected.

As might be further anticipated from the data in Table I, the isomeric methanoannulenylcarbene 38 also undergoes carbene–carbene rearrangement in solution. Thus, in our earliest work with the methanoannule-

Scheme II

(21) M. J. S. Dewar and C. C. Thompson, Jr., *J. Am. Chem. Soc.*, **87**, 4414 (1965); M. J. S. Dewar, G. L. Gleiter, and C. C. Thompson, Jr., *ibid.*, **88**, 1349 (1966).
(22) U. H. Brinker and W. M. Jones, *Tetrahedron Lett.*, 577 (1976).
(23) R. A. LaBar and W. M. Jones, *J. Am. Chem. Soc.*, **95**, 2359 (1973).
(24) P. H. Gebert, R. W. King, R. A. LaBar, and W. M. Jones, *J. Am. Chem. Soc.*, **95**, 2357 (1973).

nylcarbenes, it was found that generation of 38 from thermolysis of its tosylhydrazone salt in refluxing diglyme gave 50–60% of a mixture of hydrocarbons 48 and 49, hydrocarbons that, as mentioned above, were also formed from the ketone tosylhydrazone salt 39. Interestingly, to date none of the hydrocarbons 47 (syn
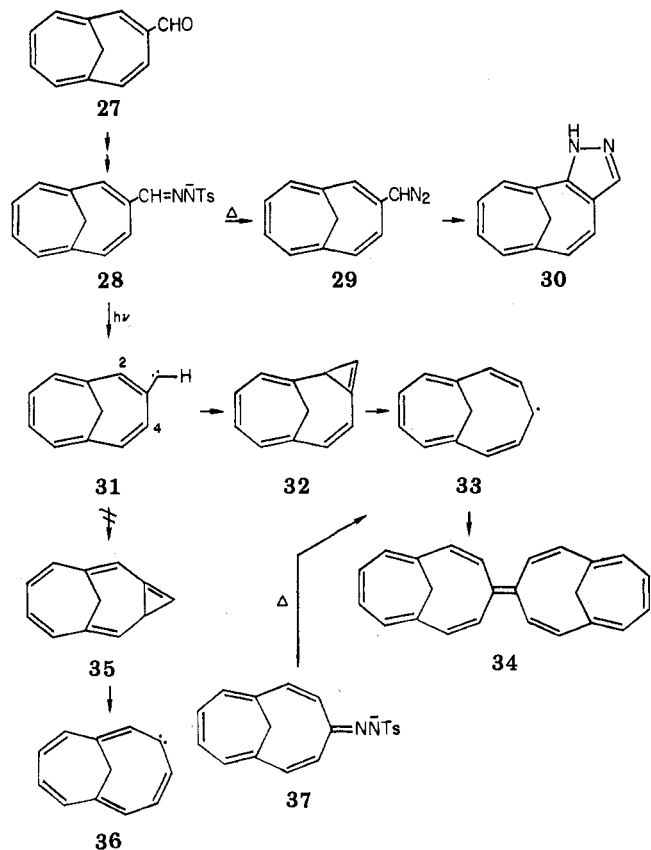
and anti) that are formed from pyrolysis of **46** and that would result from closure of **38** at C-3 have been observed. From this it would appear that this rearrangement is also highly regiospecific. Although a calculated localization energy is not available for C-1, preferential closure at this point is not surprising since the methano bridge might reasonably be expected to exert a rate-enhancing influence at this carbon.

## Mechanism of Type I Carbene–Carbene Rearrangements in Solution

In discussing the mechanism of type I carbene–carbene rearrangements, three questions will be addressed: (1) can a nitrogen-containing molecule be excluded as the rearranging species; (2) what is known about the multiplicity of the rearranging carbene; and (3) what evidence is there for a distinct intermediate? Substituent effects will also be briefly mentioned.

Very early in our work on this subject it was recognized that what appeared to be carbene–carbene rearrangements could, in reality, be rearrangements of nitrogen-containing carbene precursors. That this probably is not the case was shown in the following way.

When a carbene is generated from a tosylhydrazone salt, the last nitrogen-containing intermediate is a diazoalkane. Thus, rearrangement of a nitrogen-containing intermediate from benzotropone tosylhydrazone salt would presumably give, at some point just prior to β-naphthylcarbene, β-naphthyldiazomethane (**50**).
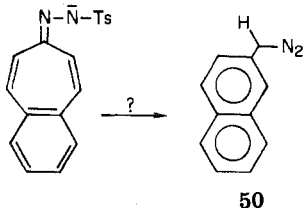
Scheme III
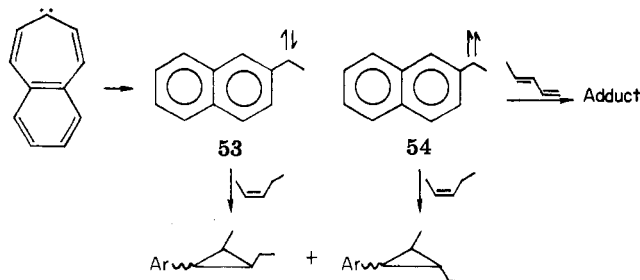
Now, it is well known that diazoalkanes are readily trapped with dipolarophiles such as dimethyl fumarate, and, in fact, heating the sodium salt of β-naphthaldehyde tosylhydrazone at 105 °C in the presence of dimethyl fumarate gave the expected pyrazoline **51**.
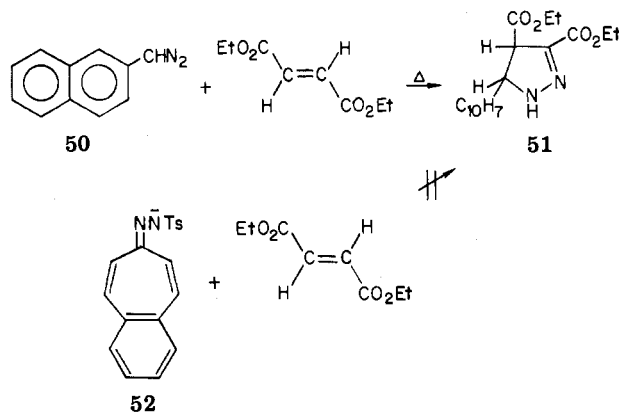
Thus, if a nitrogen-containing intermediate were rearranging to β-naphthyldiazomethane, and if an added dipolaraphile did not interrupt the rearrangement, then heating **52** in the presence of dimethyl fumarate should give pyrazoline **51**. In fact, pyrolysis of **52** at 105 °C in the presence of dimethyl fumarate gave only β-naphthylcarbene products; no trace of the pyrazoline was detected.[18] From this it is clear that β-naphthyldiazomethane is not an intermediate in the rearrangement process.

In principle, the carbene that undergoes rearrangement in a type I carbene–carbene rearrangement could be either a singlet or triplet. Evidence that it probably is a singlet was obtained by studying the effect of added substrates on the stereochemistry of the addition of rearranged β-naphthylcarbene (from the benzotropone tosylhydrazone salt **52**) to *cis*-2-pentene.[26] The arguments used are as follows.

It is known that singlet carbenes add stereospecifically to alkenes while triplet additions are nonspecific. However, there is also evidence that singlet and triplet arylcarbenes interconvert[27] fairly rapidly. Thus, if interconversion of singlet and triplet β-naphthylcarbenes were competitive with addition to an alkene, it is clear from Scheme III that the reaction with *cis*-2-pentene should not be 100% stereospecific regardless of whether the singlet–triplet manifold were entered at **53** or **54**. Now, however, if the manifold were entered at the singlet, and if reaction of the singlet with *cis*-2-pentene were competitive with crossing to the triplet,

(25) U. Brinker, R. W. King, and W. M. Jones, *J. Am. Chem. Soc.*, **99**, 3175 (1977).
(26) K. E. Krajca and W. M. Jones, *Tetrahedron Lett.*, 3807 (1975).
(27) Cf. G. L. Closs, *Top. Stereochem.*, **3**, 193 (1968).

Scheme IV
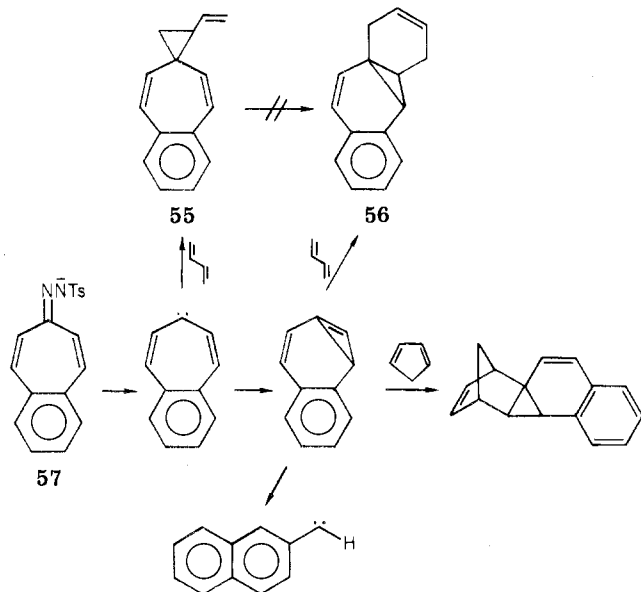
then addition of a second substrate which trapped the triplet carbene before it could either react with the alkene or revert back to singlet should cause the reaction to become stereospecific. Although these restrictions are more extreme than is actually necessary,[28] the stereospecificity of the addition of β-naphthylcarbene to *cis*-2-pentene substantially increased with the addition of either oxygen or 1,3-pentadiene. From this it would appear that β-naphthylcarbene is initially formed as a singlet, probably, though not necessarily, from a singlet precursor.

Evidence for the existence of a distinct intermediate in type I carbene–carbene rearrangements was obtained by generating annelated cycloheptatrienylidenes in the presence of effective Diels–Alder 1,3-dienes.[20] Under these conditions, rearrangement is suppressed, and substantial yields of Diels–Alder adducts of bicyclo-[4.1.0]heptatrienes (Scheme IV) are formed. That these products probably arise from cycloaddition of cyclopropenes to dienes, rather than from rearrangement of some other initially formed adduct, was shown in two ways. First, in at least one case, the expected cycloheptatrienylidene adduct 55 was also isolated and shown to be stable to the reaction conditions. Second, one of the intermediate bicyclo[4.1.0]heptatrienes (59)
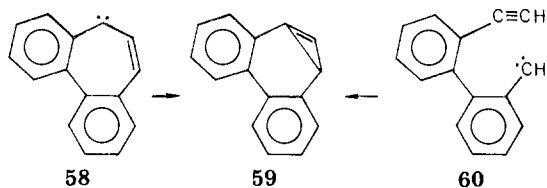
was independently synthesized by intramolecular addition of a carbene to a triple bond.[29] The products from reaction of dienes with the bicyclo[4.1.0]heptatriene derived from 58 and 60 were identical.

Finally, to conclude the discussion of the mechanism, brief mention should be made of the very limited effort that has been expended on the question of the effect of substituent groups on carbene–carbene rearrange-

ments in solution. To our knowledge, the one meaningful experiment that has been reported in this phase[30] is a study[8] of the rearrangement of 2-methyl-4,5-benzocycloheptatrienylidene to the two isomeric
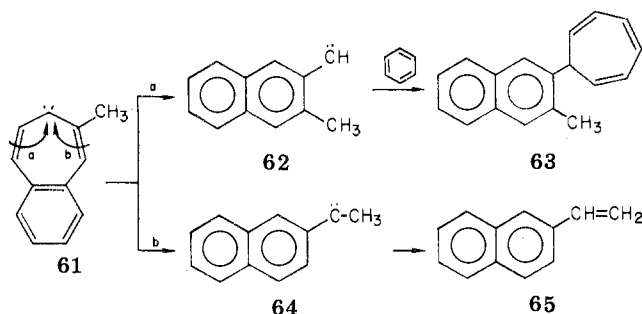
carbenes 62 and 64. By measuring the ratio of 63 to 65 (neither rearrangement is reversible under the reaction conditions) it was concluded that methyl exerts a modest accelerating effect on the rearrangement.

Concluding Remarks

Although type I carbene–carbene rearrangements in solution in which carbon is the migrating atom have been limited to date to the interconversion of aryl and aromatic carbenes, on paper any vinylcarbene can undergo this rearrangement to give a new vinylcarbene. However, in practice, it is unlikely that rearrangement will actually occur unless certain rather specific criteria are met. In the first place, closure to the cyclopropene obviously must be rapid relative to other reactions, either intramolecular or intermolecular. Furthermore, and of equal importance, under the reaction conditions the cyclopropene intermediate must open to a new carbene. Without knowing the precise mechanism of this process, it is impossible to predict under just what circumstances this requirement will be met. However, at the very least the cyclopropene must be of an energy that is within a few kilocalories of the carbene to which it is to open. In principle this could be achieved by either lowering the energy of the carbene(s) (relative to the cyclopropene) or raising the energy of the cyclopropene. The future of carbene–carbene rearrangements that depend on lowering the energy of the carbene(s) will probably be limited to the interconversion of aryl and aromatic carbenes. In these systems the energy of the two carbenes is lowered by aromaticity that is not available to the cyclopropene. However, there is no reason why this should be limited to carbocyclic systems, although some heterocyclic systems apparently have an extra side reaction[32] (fragmentation) that is not available to carbocyclics.

To our knowledge, the second potential type of perturbation—raising the energy of the cyclopropene—that could lead to type I carbene–carbene rearrangements has not yet been explored. Although it is easy to imagine systems that might meet this requirement, generation of the required carbenes may be another matter indeed.

(28) For a complete discussion see ref 26.
(29) J. P. Mykytka and W. M. Jones, *J. Am. Chem. Soc.*, **97**, 5933 (1975).
(30) The effect of substituent groups on multiple rearrangements of arylcarbenes in the gas phase and application of HOMO–LUMO theory to rationalize these effects have been reported.[6,31]
(31) C. Mayor and C. Wentrup, *J. Am. Chem. Soc.*, **97**, 7467 (1975).
(32) R. V. Hoffman and H. Shechter, *J. Am. Chem. Soc.*, **93**, 5940 (1971).

Transition-Metal Thiocarbonyls and Selenocarbonyls

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Since the end of the nineteenth century carbon monoxide has been known to bond to transition metals in low oxidation states to form metal carbonyls.[1] However, similar molecules containing the isoelectronic CS and CSe ligands have only been discovered in the past 10 years. One of the chief reasons for the relatively late development of the chemistry of transition-metal thio- and selenocarbonyls is undoubtedly the instability of CS and CSe compared to CO. Carbon monosulfide is a well-characterized species in the upper atmosphere[2] and has been shown to be intermediate in the photolysis and combustion of CS_2.[3] It can be produced in gram quantities in the laboratory by passing a high-voltage ac discharge through CS_2 in a vaccum flow system.[4] However, above −160 °C, a black-brown CS polymer is formed, and the polymerization often occurs explosively. Despite this difficulty, numerous spectroscopic studies have been carried out on the CS monomer.[5] Carbon monoselenide appears to be even more unstable since it has thus far eluded isolation,[6] although its electronic spectrum has been recorded.[7]

It is evident that CS can be stabilized by coordination to many transition metals, and well over 100 thiocarbonyl complexes have been reported, encompassing all the group 6B, 7B, and 8 metals, with the exception of technetium and palladium.[8] Metal selenocarbonyls are still extremely rare and are at present restricted to complexes of chromium, manganese, rhenium,[10] and ruthenium.[11] While the vast majority of metal thiocarbonyls and all the known metal selenocarbonyls contain terminal CX (X = S, Se) ligands, there are a few examples of thiocarbonyls with thioketonic and end-to-end CS bridging groups. X-ray studies have established that the bonding of the terminal CX[11,12] and thioketonic ligands[13] is similar to that in analogous metal carbonyls, i.e., coordination through carbon and, in the case of the terminal CX groups, linear metal–C–X linkages.

Owing to the isoelectronic nature of CO, CS, and CSe, there has been considerable interest in the comparative bonding properties of these three ligands. Molecular orbital calculations and PES measurements on CS itself and on several metal thiocarbonyl complexes have indicated that CS is a better σ-donor and π-acceptor ligand than CO.[14] The molecular orbitals for CO and CS are compared in Figure 1. The 7σ donor orbital of CS is at higher energy than the 5σ donor orbital of CO, while the 3π (π*) acceptor level of CS is at lower energy than the 2π (π*) acceptor level of CO. It should also be mentioned that the 7σ level of CS is significantly antibonding in character. At the present time there are no molecular orbital data available for CSe or any metal selenocarbonyl complex. However, ^{13}C NMR measurements on several series of group 6B and group 7B chalcocarbonyl complexes indicate that CSe is a better electron-withdrawing (σ-donor vs. π-acceptor) ligand than CS.[15,16] The above results lead one to expect that metal–CX bonds should be appreciably stronger than metal–CO bonds in view of the synergistic interaction believed to be operative for this type of ligand.[17,18]

The objectives of this Account are (1) to illustrate the currently available synthetic routes to metal thio- and

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