Carbene–Carbene Rearrangements[1]

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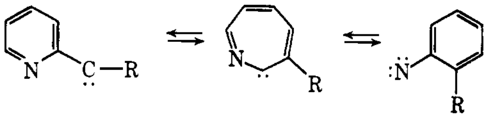
Abstract: Phenylcarbene and diphenylcarbene both undergo carbene–carbene rearrangements in the gas phase above 250° to give cycloheptatrienylidene and 2-phenylcycloheptatrienylidene, respectively. These aromatic carbenes have been detected by formation of their dimers, heptafulvalene and 2,2′-diphenylheptafulvalene (the first recorded stable heptafulvalene). *p*-Methylphenylcarbene also undergoes this rearrangement at 250° as evidenced by formation of the corresponding dimethylheptafulvalene. 2-Phenylcycloheptatrienylidene (generated either from diphenylcarbene or 2-phenyltroponetosylhydrazone sodium salt) undergoes further rearrangement to give *o*-phenylphenylcarbene which closes to fluorene. 4-Phenylphenylcarbene and 4-methylcycloheptatrienylidene undergo fourfold and fivefold carbene–carbene rearrangement sequences to give fluorene and a mixture of benzocyclobutene and styrene, respectively. Photolytically generated *o*-, *m*-, and *p*-methylphenylcarbene undergo multiple carbene–carbene rearrangements in the gas phase at room temperature (in very low yields). They do not undergo these rearrangements in solution. Whereas most carbene–carbene rearrangements to date have been limited to the gas phase, 4,5-benzocycloheptatrienylidene undergoes facile carbene–carbene rearrangement, even at room temperature. The rearranged carbene shows chemical properties identical to β-naphthylcarbene generated from β-naphthyldiazomethane. Rearrangement of a carbene precursor was excluded. Carbene–carbene rearrangements have been studied in a number of methyl substituted naphthylcarbenes and it has been found that the rearrangement occurs preferentially to the bond of highest bond order. This is consistent with a cyclopropene mechanism for the rearrangement and not consistent with a mechanism similar to the Wolff rearrangement. The cyclopropene mechanism is further supported by the facile rearrangement of 4,5-benzocycloheptatrienylidene and by the effect of a methyl substituent on the direction of 4,5-benzocycloheptatrienylidene contraction.

In contrast to the impressive histories of carbonium ion, carbanion, and free-radical rearrangements, the first nontrivial carbene-carbene rearrangement[3] was recorded less than 10 years ago with the report from Shechter's group[5] in 1965 that the pyrolysis of *o*-methylphenyldiazomethane gave, as one product, styrene. To explain this surprising result, a double carbene–carbene rearrangement was proposed.

Not until 1968 did the next report of a carbene–carbene rearrangement appear with the first of a series of elegant studies by the research group of Strausz[6] on the migration of oxygen to a carbene site.[7] In the same year, both Crow and Wentrup[8,9] as well as Sundberg[10] and his group published initial reports on the chemistry of pyridylcarbene and phenylnitrene for which both carbene–carbene and carbene–nitrene[11] rearrangements have been postulated.



These were followed by a report[13] of the base-induced contraction of ferrocenyl cycloheptatrienyl fluoroborate and a number of examples of carbene–carbene rearrangements of simple arylcarbenes[14–16] including direct evidence for the gas-phase interconversion of phenylcarbenes and cycloheptatrienylidenes.

At this time, we present a full account of our work to date on the interconversion of aryl- and aromatic carbenes.

Gas-Phase Interconversions. Phenylcarbene undergoes facile rearrangement to cycloheptatrienylidene in the gas phase at temperatures ranging from 250–600°. Evidence for the rearrangement rests on the formation

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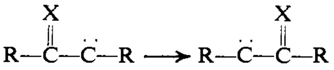
(1) Portions taken from the Ph.D. dissertations of J. A. Myers and K. E. Krajca and from the M. S. thesis of T. L. Davis.

(2) (a) University of Florida Postdoctoral Fellow; (b) National Science Foundation Trainee, 1965–1969; (c) on temporary leave from Tokyo University.

(3) The carbene–carbene rearrangement may be conveniently represented in essentially the same way as carbonium ion, carbanion, and free radical rearrangements, *i.e.*, simply as migration of a group to the reaction site with generation of a new carbene.[4] Furthermore, as in the case of the more conventional rearrangements, this notation carries



$$R-\overset{\overset{\displaystyle X}{\|}}{C}-\ddot{C}-R \longrightarrow R-\ddot{C}-\overset{\overset{\displaystyle X}{\|}}{C}-R$$

with it no mechanistic implications. It, of course, differs from the other rearrangements in that more than one bond must be broken and remade.

(4) For a different type of carbene–carbene rearrangement, see L. Skattebøl, *Tetrahedron*, 1107 (1967).

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

(6) G. Frater and O. P. Strausz, *ibid.*, **92**, 6654 (1970); D. E. Thornton, R. G. Gosavi, and O. P. Strausz, *ibid.*, **92**, 1768 (1970); I. G. Csizmadia, J. Gont, and O. P. Strausz, *ibid.*, **90**, 7360 (1968).

(7) For an alternative to a direct carbene–carbene rearrangement through the proposed oxirene intermediate, see R. L. Russell and F. S. Rowland, *ibid.*, **92**, 7508 (1970).

(8) W. D. Crow and C. Wentrup, *Tetrahedron Lett.*, 6149 (1968).

(9) W. D. Crow and C. Wentrup, *Chem. Commun.*, 1387 (1969).

(10) R. J. Sundberg, W. J. Adams, R. H. Smith, and D. E. Blackburn, *Tetrahedron Lett.*, 777 (1968); R. J. Sundberg, B. P. Das, and R. H. Smith, Jr., *J. Amer. Chem. Soc.*, **91**, 658 (1969); R. J. Sundberg and S. R. Suter, *J. Org. Chem.*, **35**, 827 (1970).

(11) The first example of a reaction that may involve a nitrene–carbene rearrangement was reported in 1958 by Huisgen.[12]

(12) R. Huisgen, D. Vossins, and M. Appl, *Chem. Ber.*, **91**, 1 (1958).

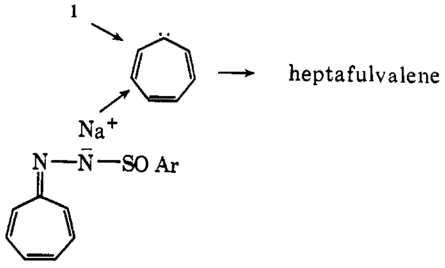
(13) P. Ashkenasi, S. Lupan, A. Scharz, and M. Cais, *Tetrahedron Lett.*, 817 (1969).

(14) R. C. Joines, A. B. Turner, and W. M. Jones, *J. Amer. Chem. Soc.*, **91**, 7754 (1969).

(15) J. A. Myers, R. C. Joines, and W. M. Jones, *ibid.*, **92**, 4740 (1970).

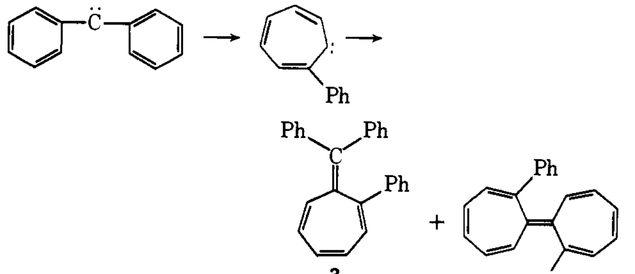
(16) W. J. Baron, M. Jones, Jr., and P. P. Gaspar, *ibid.*, **92**, 4739 (1970); P. O. Schissel, M. E. Kent, M. J. McAdoo, and E. Hedaya, *ibid.*, **92**, 2147 (1970); C. Wentrup and K. Wilczek, *Helv. Chim. Acta*, **53**, 1459 (1970).

of known heptafulvalene[17] which is essentially the sole product of both solution[18] and pyrolysis-tube (conditions of our reaction were 250°, 40 mm from N_2 stream) decompositions of the sodium salt of tropone tosylhydrazone. Evidence that some and probably all of the dimerization occurs in the gas phase was obtained by decomposing a mixture of the sodium salts of benzaldehyde tosylhydrazone and *p*-methylbenzaldehyde tosylhydrazone[19] and isolating a mixture of heptafulvalene, dimethylheptafulvalene, and a material with the properties of monomethylheptafulvalene.



Although the presence of cycloheptatrienylidene and phenylcarbene (as well as phenyldiazomethane) in the gas phase would suggest formation of phenylheptafulvene, none was found. While it is tempting to attribute this to a low concentration of phenylcarbene suggesting an unfavorable equilibrium between phenylcarbene and cycloheptatrienylidene, it is also quite possible that phenylheptafulvene is not stable to the reaction or work-up conditions.

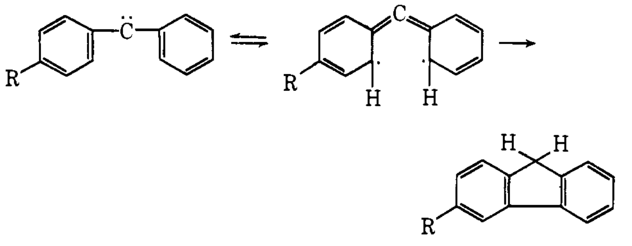
In contrast to phenyldiazomethane, decomposition of diphenyldiazomethane gave in addition to fluorene (origin discussed below) both triphenylheptafulvene (**3**) and diphenylheptafulvalene (**4**) (total yield of dimers, 30–35%). For structure proofs including alternate synthesis of **4**, see the Experimental Section.



3 **4**

The near absence of stilbenes and tetraphenylethylenes (or triphenylheptafulvene) from the pyrolysis of the sodium salts of the tosylhydrazones of tropone and 2-phenyltropone[21] suggests an equilibrium between aryl- and aromatic carbenes that lies well on the side of the cycloheptatrienylidene (see the section on rearrangements in solution). However, this argument is weakened by our ignorance of the role of the diazoalkane in the formation of ethylenes from the pyrolysis of phenyldiazomethanes; *i.e.*, to our knowledge the tendency of arylcarbenes to dimerize is unknown.

Multiple Carbene–Carbene Rearrangements. In the gas phase, diphenylcarbene gives, in addition to **3** and **4**, 25–30% fluorene (**6**). Although this has been identified a number of times[22,23] as a product from thermally produced diphenylcarbene, in only one instance[23] was a specific reaction mechanism proposed. Formation of **3** and **4** as well as the reported interconversion of pyridylcarbenes[8,9] and phenylnitrene[10] suggested as an alternative mechanism a sequence of two carbene–carbene rearrangements. This was a particularly interesting alternative since the second rearrangement is a contraction of a cycloheptatrienylidene, a reaction that was not conclusively identified in our hands[21] in our work on cycloheptatrienylidene. The double carbene–carbene mechanism was supported and the mechanism proposed by Harrison and Lossing was excluded as a tenable possibility when it was found that methyl or methoxy label in the para position of the starting carbene appeared *only* in the 2 position of the fluorene product.[24] As one possible alternative to double carbene–carbene rearrangement, the intermediate cycloheptatrienylidene could be by-passed by a sequence involving only two carbenes and rearrangement of the vinylcyclopropene.[25] Very strong evidence against this as the *sole* source of fluorene was obtained



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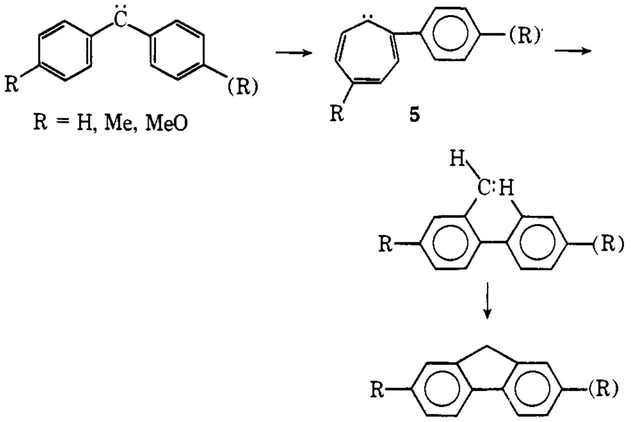

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(17) W. von E. Doering in "Theoretical Organic Chemistry. The Kekule Symposium," Academic Press, New York, N. Y., 1959, p 44.

(18) W. M. Jones and C. L. Ennis, *J. Amer. Chem. Soc.*, **91**, 6391 (1969).

(19) At higher temperatures, this tosylhydrazone undergoes multiple rearrangements giving styrene and benzocyclobutene.[16,20] At 250° these rearrangements were not observed.

(20) E. Hedaya and M. E. Kent, *J. Amer. Chem. Soc.*, **93**, 3283 (1971).

(21) Low yields of stilbene (less than 2%) were observed by Wentrup and Wilczek[16] from the pyrolysis of the sodium salt of tropone tosylhydrazone. We have observed traces of stilbenes to which we can ascribe no real significance since the runs that were examined were made on tosylhydrazone made from tropone synthesized by selenium dioxide oxidation of cycloheptatriene, a method which we have found also gives traces of benzaldehyde.

(22) H. Staudinger and R. Engle, *Ber.*, **46**, 1437 (1913); F. O. Rice and J. D. Michaelsen, *J. Phys. Chem.*, **66**, 1535 (1962).

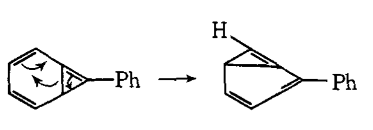
(23) H. D. Harrison and F. P. Lossing, *J. Amer. Chem. Soc.*, **82**, 1052 (1960).

(24) Wentrup and Wilczek[16] have made a similar study and have arrived at the same conclusion.

(25) This same type of rearrangement has been suggested[26] as a possible explanation for the results of the deoxygenation of aromatic nitro compounds with phosphites.

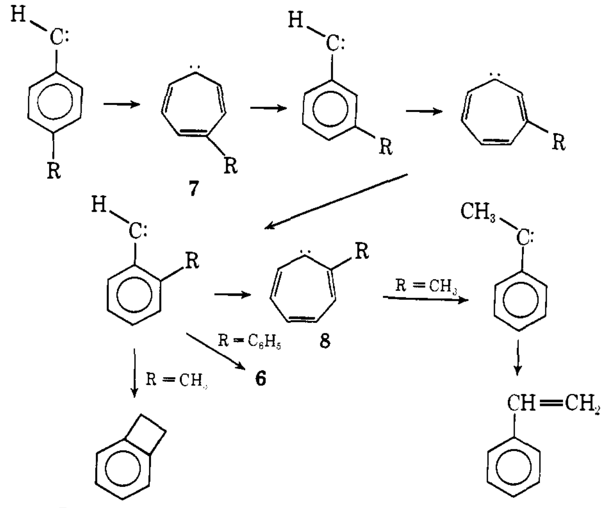
(26) J. I. G. Cadogen, *Quant. Rev., Chem. Soc.*, 222 (1968).

by generating 2-phenylcycloheptatrienylidene **5** under the conditions of the reaction and observing fluorene formation. Thus, if it is assumed that **3** and **4** arise from phenylcycloheptatrienylidene, then at least some of the fluorene *must* come from the double carbene–carbene rearrangement sequence.[27]



Pyrolysis of *p*-phenylphenyldiazomethane was also found to give a low yield of fluorene, a product which suggests a fourfold carbene–carbene rearrangement sequence. However, in view of the more detailed work in a number of laboratories on multiple rearrangements of *p*-methylphenylcarbene, this reaction was given only cursory attention.

Pyrolysis of the sodium salt of *p*-methylbenzaldehyde tosylhydrazone (at 250°) was reported from these laboratories[14] to give dimethylheptafulvalene. However, shortly thereafter, it was reported[16,20] that higher temperature (420–700°) pyrolysis of *o*-, *m*-, and *p*-methylphenyldiazomethane gave, in up to 50% yield, benzocyclobutene and styrene. To explain these products, a fourfold and a sixfold carbene–carbene rearrangement sequence were suggested. Although, from the initial results, the cycloheptatrienylidenes could be by-passed (by the vinylcyclopropene mechanism) the interconversions of methylphenylcarbenes and methylcycloheptatrienylidenes have now received attention in at least four laboratories and all results to date support the multiple carbene–carbene sequence including involvement of cycloheptatrienylidenes. Thus, Shechter[5] has carried out a detailed study on the conversion of *o*-methylphenylcarbene to styrene and has excluded a number of possible mechanisms. Hedaya[20] has tagged the carbene carbon of *p*-methylphenylcarbene and has found the position of the tag in both benzocyclobutene and styrene to be consistent with the multiple carbene–carbene sequence. Finally, we have entered the sequence at carbenes **7** and **8** and have found the products and their ratios[28] to be consistent with the proposed sequence. It should be noted that the rearrangements of the methyl-substituted cycloheptatrienylidenes provide further evidence for the reversibility of the arylcarbene–aromatic carbene rearrangement.



Finally, in the area of multiple rearrangements, we have found that photochemically generated methylphenylcarbenes also undergo multiple carbene–carbene rearrangements. Thus, slow volatilization (2 Torr) of *o*-, *m*-, or *p*-phenyldiazomethane from a reservoir at 0° through an irradiated (Hanovia, 550 W) Pyrex or quartz tube (room temperature) into a liquid nitrogen trap gave, in addition to starting material, low yields of benzocyclobutene and styrene. Product ratios from the photolysis experiments are summarized in Table I. It is interesting that the meta and para isomers gave a slight predominance of styrene with product ratios very similar to the high temperature pyrolyses. Furthermore, as in the pyrolyses, the ortho isomer showed an anomolous behavior giving a predominance of benzocyclobutene with a ratio essentially the same as that observed by Shechter[5] at 250° and considerably lower than the higher temperature runs. The reason for the anomolous behavior of the ortho isomer is unknown.

Table I. Vapor-Phase Photolysis of the Tolyldiazomethanes[a]

Starting material	Benzocyclobutene/[b] styrene
p-Tolyldiazomethane	0.5
m-Tolyldiazomethane	0.7
o-Tolyldiazomethane	1.4

[a] Irradiation of the tolyldiazomethanes was carried out at 2 mm and 30°. [b] Assayed by nmr.

From all of the above results, it is apparent that arylcarbenes and cycloheptatrienylidenes undergo interconversions in the gas phase at temperatures ranging from 700° to as low as 250° in thermal reactions and at room temperature photolytically (although a thermally excited ground state could be involved).[29] Furthermore, although the reversibility of the rearrangement has been firmly established, the relative energies of the aromatic carbenes and arylcarbenes cannot be set.

Carbene–Carbene Rearrangements in Solution. All of the carbene–carbene rearrangements discussed in the previous section were carried out in the gas phase and, with the exception of the photolyses, at relatively high temperatures. Furthermore, with the exception of aromatic carbene dimerizations, in no case has it been possible to examine intermolecular reactions of any of the rearranged carbenes. We therefore undertook a study of carbene–carbene rearrangements in solution.

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(27) It is interesting that the ratio of diphenylheptafulvalene to fluorene in the reaction of phenylcycloheptatrienylidene is much higher than it is in the diphenylcarbene reaction. This probably simply reflects a higher localized concentration of aromatic carbenes in the former.

(28) At 450°, carbene **7** (R = CH_3) gives benzocyclobutene and styrene in a ratio of about 1 : 1. Carbene **8** (R = CH_3) gives styrene with no detectable benzocyclobutene. Owing to instability of intermediates and our inability to obtain the latter tosylhydrazone in crystalline form, the precursors to this carbene were not as fully characterized as would have been desirable. This result must therefore be taken as tentative (see the Experimental Section).

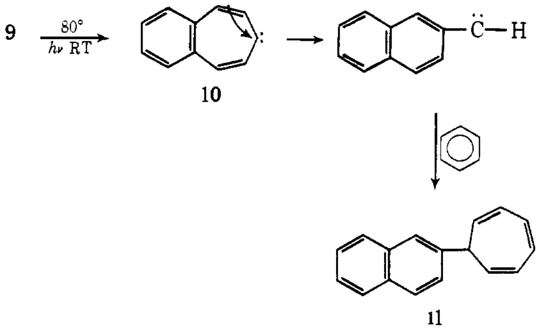
(29) The possibility of vibrationally excited states is supported by the fact that photolysis of dilute solutions of *p*-methylphenyldiazomethane in hexafluorobenzene and octafluorocyclobutane showed no trace of benzocyclobutene or styrene.

For this study, the phenylcarbene–cycloheptatrienylidene reaction was taken as the prototype. Phenylcarbene was generated in diglyme under conditions (165°) where the salt of tropone tosylhydrazone gives heptafulvalene and the reaction mixture was carefully examined for cycloheptatrienylidene dimer. No trace was found; the only products were benzalazine and a material which is surely the set of diglyme–phenylcarbene insertion products. Cycloheptatrienylidene was then generated under conditions where phenylcarbene gives clean reaction with solvent (diglyme, up to 210°) and the reaction mixture carefully analyzed for phenylcarbene insertion products. No trace was found, the only recognizable product being heptafulvalene.

The failure of phenylcarbene to expand in solution is probably due to a favorable competitive intermolecular reaction with solvent. Cycloheptatrienylidene, on the other hand, is very unreactive with most solvents, preferring to simply dimerize. Thus, its failure to contract requires an activation energy high enough to allow dimerization to dominate.

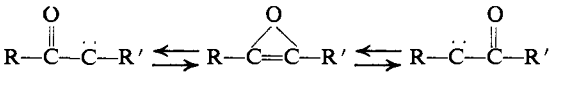
As one possible way to reduce the activation energy for contraction while hopefully retaining enough of the low reactivity of the aromatic carbene to prevent extensive reaction with solvent, cycloheptatrienylidene was monoannelated[30,32] and its chemistry studied. This carbene (**10**) was generated from the sodium salt of benzotropone tosylhydrazone (**9**).

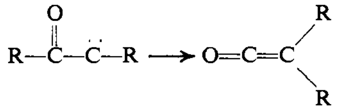
Pyrolysis and photolysis of the sodium salt were examined under a variety of conditions. Temperatures in the range of 80–100° were required to effect thermal decomposition. There were no temperature restrictions on the photolyses although the extent of rearrangement appears to be temperature dependent. Rearranged naphthylcarbene was detected by its reaction products with solvent. For example, decomposition of the salt in benzene (80° thermal, 30° photolytic) gave naphthylcycloheptatriene (**11**) as the major product (97 and 59%, respectively). Formation of naphthylcycloheptatriene suggests a carbene–carbene rearrangement followed by reaction of the rearranged carbene with solvent. Formation of the insertion product β-naphthylcyclohexylmethane (51%) from the decomposition of **9** in cyclohexane provided supporting evidence[33] for production of the rearranged carbene.



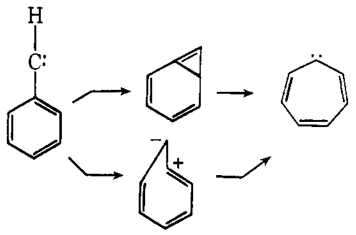
To exclude rearrangement of a carbene precursor, β-naphthyldiazomethane and an equivalent amount of benzotropone tosylhydrazone salt were independently heated in benzene under identical conditions in the presence of an equimolar amount of dimethyl fumarate. As expected, β-naphthyldiazomethane gave as the primary product (50%) an oil showing all of the properties anticipated for the pyrazoline. In contrast, the sodium salt of benzotropone tosylhydrazone gave no detectable trace of pyrazoline; only products believed to be diglyme insertion products of β-naphthylcarbene were formed.

Mechanism of Carbene–Carbene Rearrangements. Carbonyl carbenes have been found to undergo two fundamentally different types of reaction. In the one, ring closure to an oxirene is believed to occur.[6] The oxirene, an antiaromatic ring system, is then thought to open to give a new carbene. In the other, the well-known Wolff rearrangement occurs with formation of a ketene. However, unlike carbonylcarbenes for which these two mechanisms give different products, when applied to the interconversion of arylcarbenes and aromatic carbenes, they give the *same* product.[34]

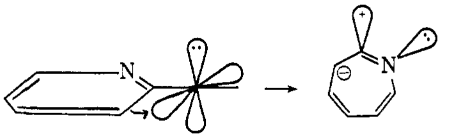




$$R-\overset{\overset{\textstyle O}{\|}}{C}-\ddot{C}-R \longrightarrow O{=}C{=}C\begin{matrix}R\\R\end{matrix}$$



Drawing from acyclic systems, the Wolff mechanism would be expected to be favored by appropriately positioned electronegative elements with nonbonded electrons (*e.g.*, α-pyridylcarbene[8,9]); the electronegativity would favor a conformation with the filled orbital conjugated with the π system leaving the vacant orbital aligned with the σ framework, and the nonbonded pair could stabilize the resulting zwitterion. Whether it would be favored enough to compete with the cyclopropene mechanism remains an open question.



On the other hand, the instability of the bent vinyl

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(30) Monoannelation is known to substantially decrease the stability of the tropyl cation[31] but it should have little effect on the stability of the intermediate cyclopropene. Thus, if the stability of the carbene parallels the carbonium ion and if the rate of contraction is reflected in the relative stability of the intermediate, then benzocycloheptatrienylidene should contract faster than cycloheptatrienylidene.

(31) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," Wiley, New York, N. Y., 1961.

(32) The chemical behavior of di- and triannelated cycloheptatrienylidene is very similar to that of diarylcarbenes: I. Moritani, S. Murahashi, M. Nishino, Y. Yamamoto, K. Itoh, and N. Mataya, *J. Amer. Chem. Soc.*, **89**, 1259 (1967); I. Moritani, *et al.*, *Tetrahedron*, **27**, 5131 (1971), and references cited.

(33) *Cf.* W. Kirmse, "Carbene Chemistry," Academic Press, New York, N. Y., 1964; J. Hine, "Divalent Carbon," Ronald Press, New York, N. Y., 1964.

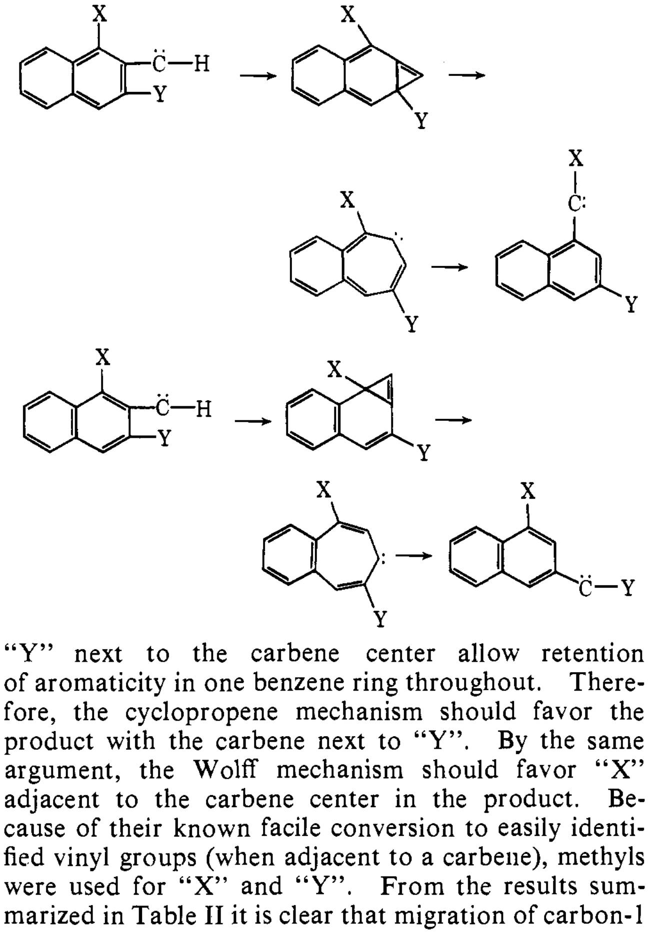
(34) Wentrup[35] has suggested a ring opened diradical as a third alternative for nitrene–carbene rearrangements.

(35) C. Wentrup, *Tetrahedron*, **26**, 4965 (1970).

cation makes the Wolff mechanism an intuitively unattractive alternative, especially for the nonheterocyclic systems. As a result, natural bias lies in favor of the cyclopropene mechanism.

Experimentally, these two mechanisms differ in that the cyclopropene mechanism should be favored by high double-bond character whereas the Wolff mechanism should be retarded. We therefore undertook to assess the importance of bond order in the interconversion of aryl and aromatic carbenes by studying the gas-phase carbene–carbene rearrangement of a series of substituted naphthylcarbenes.

To illustrate the method, consider the cyclopropene mechanism for the rearrangement of a labeled 2-naphthylcarbene. Rearrangement to give an intermediate with "X" adjacent to the carbene center requires a "pseudo-aromatic" series of intermediates. On the other hand, the two rearrangements required to place "Y" next to the carbene center allow retention of aromaticity in one benzene ring throughout. Therefore, the cyclopropene mechanism should favor the product with the carbene next to "Y". By the same argument, the Wolff mechanism should favor "X" adjacent to the carbene center in the product. Because of their known facile conversion to easily identified vinyl groups (when adjacent to a carbene), methyls were used for "X" and "Y". From the results summarized in Table II it is clear that migration of carbon-1 from carbon-2 to the carbene center in 3-methyl-2-naphthylcarbene must be a facile process. In contrast, the complete absence of 1-vinylnaphthalene from 1-methyl-2-naphthylcarbene or 2-vinylnaphthalene from 2-methyl-1-naphthylcarbene point to no migration of carbon-3 to a carbene center on carbon-2 or carbon-9 to a carbene center on carbon-1. In other words, net cleavage of the bond of high bond order is observed; net cleavage of the bonds of low bond order is not.



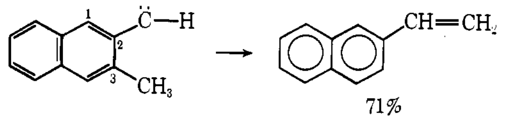
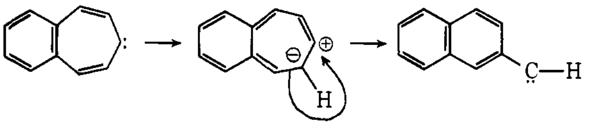


Table II. Pyrolysis of the Sodium Salts of Monomethylnaphthaldehyde *p*-Toluenesulfonylhydrazones

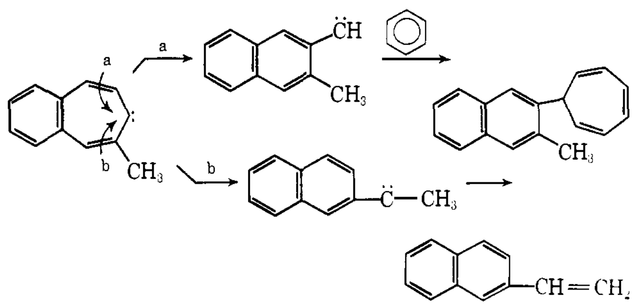
Aldehydes	Temp, °C	Yield,[a] % I[b]	II[b]	III[b]	IV[b]
4-Methyl-1-naphthaldehyde	350	0		0	
2-Methyl-1-naphthaldehyde	350		0	17.5	
1-Methyl-2-naphthaldehyde	350	0		16	
3-Methyl-2-naphthaldehyde	350		55		2.2
	300		53		4.2
	250		70.5		5.6
	200		48.5		5.9
2-Methylbenzotropone	350		24		2.5

[a] Determined by nmr and vpc. [b] Compared with authentic samples (I) 1-vinylnaphthalene; (II) 2-vinylnaphthalene; (III) naphtho[*a*]cyclobutene; (IV) naphtho[*b*]cyclobutene.

The cyclopropene mechanism is further supported by the facile contraction of benzocycloheptatrienylidene as compared with unsubstituted cycloheptatrienylidene. Thus, annelation should retard the Wolff type of mechanism (which would require a pseudo-aromatic system) while it should favor the cyclopropene mechanism since less aromaticity would be lost in forming the small ring.[36]



Finally, the effect of methyl substitution on the rate of carbene–carbene rearrangement has been cursorily examined. Thus, the salt of 2-methyl-4,5-benzotropone tosylhydrazone was synthesized and allowed to decompose in benzene solution. From the preferred formation of vinylnaphthalene compared with naphthylcycloheptatriene (3.3:1)[37] it would appear that alkyl substitution favors rearrangement.



The above work, the known[38] closure of vinylcarbenes to cyclopropenes, and the known[39] pyrolysis of

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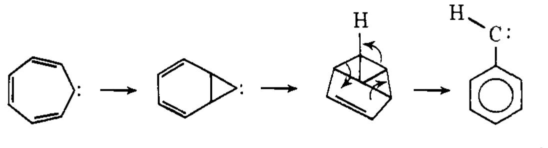
[36] Another interesting mechanism that can be written for the contraction of cycloheptatrienylidene which has not been previously discussed is essentially the Skattebøl[5] vinylcyclopropylidene–cyclopentenylidene rearrangement with cleavage of different bonds. The effect of annelation argues against this possibility since it should retard norcaradiene formation and hence the rate of contraction.



[37] Neither 3-methyl-2-naphthylcarbene nor 1-methyl-2-naphthylcarbene ring expands under the reaction conditions.

[38] G. L. Closs and L. E. Closs, *J. Amer. Chem. Soc.*, **85**, 99 (1963), and references cited.

[39] *Cf.* G. L. Closs in "Advances in Alicyclic Chemistry," Vol. 1, H. Hart and G. Karabatsos, Ed., Academic Press, New York, N. Y., Chapter 2.

cyclopropenes to give vinylcarbene-type products all point to a cyclopropene mechanism for the interconversion of arylcarbenes and aromatic carbenes. Furthermore, although it seems intuitively likely that the cyclopropene is a distinct intermediate, a concerted mechanism cannot be ruled out. If the reaction is not concerted, the activation energy for ring opening must be quite low as evidenced by the fact that benzocycloheptatrienylidene contracts to 2-naphthylcarbene at temperatures as low as room temperature. The low activation energy is not unreasonable since the energy lost in cleaving the single bond of the twisted cyclopropene (the benzobicycloheptatriene) might be of the same order of magnitude as the naphthyl resonance energy gained.[40]

Finally, if rearrangement proceeds through closure to a cyclopropene it should be pointed out that in contrast to the assumed[38] geometry for closure of vinylcarbenes, the geometry of cycloheptatrienylidenes requires contraction of a carbene in which the sp^2 orbital is anti to the double bond.

Experimental Section

General. Melting points were taken in a Thomas–Hoover Unimelt apparatus and are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn., or by Atlantic Microlab, Inc., Atlanta, Ga. Ultraviolet spectra were recorded on a Cary 14 or Cary 15 double-beam spectrophotometer using 1-cm silica cells. Infrared spectra were recorded with a Beckman TR10 or a Perkin-Elmer 337 spectrophotometer. In all cases where the KBr pellet technique was not used, sodium chloride plates were substituted. Nuclear magnetic resonance spectra were determined on a Varian A-60A high resolution spectrometer. Chemical shifts are reported in τ values from internal tetramethylsilane standard. Mass spectra were determined on a Hitachi Model RMU-6E mass spectrometer.

Analytical thin-layer chromatography was accomplished on 2 × 8 in. plates coated in these laboratories with 0.25-mm layers of E. Merck HF-254 silica gel; preparative work was conducted on 8 × 8 in. plates coated with 1.0-mm layers of HF-254 silica gel. Components were visualized by their quenching of fluorescence under uv light.

Benzaldehydes, Naphthaldehydes, and Benzophenones. Commercial benzaldehyde, *o*-, *m*-, and *p*-methylbenzaldehyde, *β*-naphthaldehyde, *p*-phenylbenzaldehyde, benzophenone, *p*-methylbenzophenone, and *p*-methoxybenzophenone were used without further purification.

3-Methyl-2-naphthaldehyde was prepared according to the method of Sultanov, Rodionov, and Schemyakin[41] by oxidation of 2,3-dimethylnaphthalene with selenium dioxide. 1-Methyl-2-naphthaldehyde, 2-methyl-1-naphthaldehyde, and 4-methyl-1-naphthaldehyde were prepared from the corresponding bromomethylnaphthalenes[42] by the procedure described by Ziegler and Tiemann.[43]

Preparation of Aldehyde Tosylhydrazones. Aldehyde tosylhydrazones were prepared in the conventional way to give benzaldehyde tosylhydrazone, mp 127–128° (lit.[44] mp 127–128°); *o*-methylbenzaldehyde tosylhydrazone, mp 139.5–140° (lit.[45] mp 143–144°); *m*-methylbenzaldehyde tosylhydrazone, mp 119–119.5° (*Anal.* Calcd for $C_{15}H_{16}N_2O_2S$: C, 62.49; H, 5.59. Found: C, 62.39; H, 5.62); *p*-methylbenzaldehyde tosylhydrazone, mp 149–151.5° (*Anal.* Calcd for $C_{15}H_{16}N_2O_2S$: C, 62.49; H, 5.59. Found: C, 62.47; H, 5.62); *β*-naphthaldehyde tosylhydrazone, mp 175° (lit.[46] mp 174°); *p*-phenylbenzaldehyde tosylhydrazone, mp 194–196° dec (*Anal.* Calcd for $C_{20}H_{18}N_2O_2S$: C, 68.56; H, 5.18. Found: C, 68.41; H, 5.23). The methyl-substituted naphthaldehyde tosylhydrazones were prepared by dissolving the aldehyde in THF (1 g/5 ml), adding an equivalent of tosylhydrazide, refluxing for 15 min, and concentrating. The residue was recrystallized from ethanol to give the following products: 3-methyl-2-naphthaldehyde tosylhydrazone, mp 190–192° (*Anal.* Calcd for $C_{19}H_{18}N_2O_2S$: C, 67.43; H, 5.36; N, 8.28. Found: C, 67.35; H, 5.42; N, 8.31); 1-methyl-2-naphthaldehyde tosylhydrazone, mp 185° (*Anal.* Calcd for $C_{19}H_{18}N_2O_2S$: C, 67.43; H, 5.36; N, 8.28. Found: C, 67.57; H, 5.40; N, 8.29); 2-methyl-1-naphthaldehyde tosylhydrazone, mp 174–175° (*Anal.* Calcd for $C_{19}H_{18}N_2O_2S$: C, 67.43; H, 5.36; N, 8.28. Found: C, 67.60; H, 5.40; N, 8.33); 4-methyl-1-naphthaldehyde tosylhydrazone, mp 158° (*Anal.* Calcd for $C_{19}H_{18}N_2O_2S$: C, 67.43; H, 5.36; N, 8.28. Found: C, 67.72; H, 5.40; N, 8.39).

Preparation of Sodium Salts of Tosylhydrazones. The sodium salts were prepared by dissolving the tosylhydrazone in dry THF (*ca.* 2 g/30 ml; THF distilled from $LiAlH_4$ and stored over CaH) and adding 1 equiv of sodium hydride (57% in mineral oil—Alfa Inorganics) slowly with stirring. Stirring was continued for an additional 15 min. Reagent-grade pentane was added (*ca.* 200 ml/30 ml THF), and the resulting precipitate filtered and stored in a dark bottle in the drybox. Most of the salts may be stored indefinitely if moisture is rigorously excluded.

Preparation of Aryldiazomethanes. *o*-, *m*-, and *p*-tolyldiazomethanes were prepared by thermolysis of the sodium salt of the appropriate tosylhydrazone using the general method of Shechter and coworkers.[47] *o*-Tolyldiazomethane: nmr ($CDCl_3$) τ 7.87 (s, 3, CH_3), 5.13 (s, 1, CHN_2), and 3.0 (m, 4, aromatic). *m*-Tolyldiazomethane: nmr ($CDCl_3$) τ 7.75 (s, 3, CH_3), 5.29 (s, 1, CHN_2), and 3.35 to 2.80 (m, 4, aromatic). *p*-Tolyldiazomethane: nmr ($CDCl_3$) τ 7.75 (s, 3, CH_3), 5.30 (s, 1, CHN_2), and 3.18 (A_2B_2, J_{AB} = 8.5 Hz, 4, aromatic); uv max (*n*-hexane), 276 nm (ϵ 22,000) and 480 nm (ϵ 27). *β*-Naphthyldiazomethane was prepared in 42% yield in the same way.

Preparation of Diaryldiazomethanes. All diaryldiazomethanes were prepared by oxidation of the hydrazone.[48] Just prior to use, the diaryldiazoalkanes were dissolved in cold pentane and decanted from any solid ketazine that may have formed. The diaryldiazomethanes used were: diphenyldiazomethane, mp 26–27° (lit.[46] mp 30°), the nmr showed a singlet at τ 2.78; 4-methyldiphenyldiazomethane, mp 54–56° (lit.[49] mp 53–55°); 4-methoxydiphenyldiazomethane, mp 51–53° (lit.[50] mp 56°).

Hot-Tube Technique. The apparatus used for the hot-tube pyrolyses consisted of a Pyrex tube (23-mm i.d., 40 cm long) maintained at the desired temperature by resistance wire. The tube was wrapped with aluminum foil and asbestos to minimize heat loss. Near the lower end of the tube a mat of glass wool was inserted to retain all nonvolatile materials and allow only gases to pass to the receiver. At the top of the tube, provisions were made for the introduction of nitrogen (metered externally at atmospheric pressure) and solid reactants *via* a solid addition tube. The lower end of the tube was fitted with a ground glass ball joint which was attached to the receiver. The pyrolysis tube was bent near the bottom joint such that the pyrolysis zone was angled about 35° from the vertical. When diazoalkanes were pyrolyzed, they were normally first dissolved in cold pentane, an inert support (Chromosorb P (dried at 250° under N_2 before use) or firebrick) was added and the pentane was removed under reduced pressure leaving the diazoalkane coated on the support. The inert support remained on the glass wool mat at the end of the column. The inside diameter of the receiver was the same as that of the column with constrictions avoided above the surface of the liquid nitrogen. The receiver, which was cooled in liquid nitrogen, was packed with glass wool to break aerosols. The receiver was attached to the vacuum line which was evacuated with a Cenco Model 91142 vacuum pump.

Pyrolysis of the Sodium Salts of Benzaldehyde and *p*-Methyl-

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[40] Based on work at 700°, Hedaya[20] has also concluded that "relatively small energy barriers separate phenylcarbene, cycloheptatrienylidene and bicycloheptatriene isomers."

[41] A. S. Sultanov, V. M. Rodionov, and M. M. Schemyakin, *J. Gen. Chem.*, **16**, 2072 (1946); *Chem. Abstr.*, **42**, 881 (1948); J. E. Shields and J. Bornstein, *Chem. Ind. (London)*, 1404 (1967).

[42] V. Vesely, F. Stursa, H. Olejnicek, and E. Rein, *Collect. Czech. Chem. Commun.*, **2**, 145 (1930); *Chem. Abstr.*, **24**, 3009 (1930); F. Mayer and A. Sieglitz, *Ber.*, **55**, 1839 (1922).

[43] K. Ziegler and P. Tiemann, *ibid.*, **55**, 3406 (1922).

[44] K. Freudenberg and F. Blümmel, *Justus Liebigs Ann. Chem.*, **440**, 51 (1924).

[45] H. Nozaki, R. Noyori, and K. Sisido, *Tetrahedron*, 20, 1125 (1964).

[46] L. Caglioti and M. Magi, *ibid.*, **19**, 1127 (1963).

[47] G. M. Kaufman, J. A. Smith, G. G. Vander Stouw, and H. Shechter, *J. Amer. Chem. Soc.*, **87**, 935 (1965).

[48] R. Baltzly, N. B. Mehta, P. B. Russell, R. E. Brooks, E. M. Grivsky, and A. M. Steinberg, *J. Org. Chem.*, 26, 3669 (1961).

[49] H. Staudinger and J. Goldstein, *Chem. Ber.*, **49**, 1923 (1916).

[50] W. Kirmse and L. Horner, *Justus Liebigs Ann. Chem.*, **625**, 34 (1959).

benzaldehyde Tosylhydrazones. In a typical experiment, 1.0 g of the sodium salt of benzaldehyde tosylhydrazone was introduced (10–15 min) into the pyrolysis tube which was maintained at a temperature of 250° at a pressure of 40 mm (from nitrogen introduced into the column at 0.5 l./min). The resulting light-beige coating on the surface of the receiver turned a deep blackish brown (without gas evolution) upon warming to room temperature. The nmr of the crude reaction mixture showed resonances typical of stilbenes (confirmed by gc; cis:trans, 1.3:1) normally corresponding to about one-third of the hydrocarbons and the remaining two-thirds showed a structured singlet at τ 4.15 characteristic of heptafulvalene. This assignment was confirmed by isolation (Alumina, activity grade II, pentane elution) and comparison of the uv with that of known heptafulvalene; λ_{max} (EtOH) 234 $m\mu$ (ϵ 22,000); and 362 (21,000). The yield was about 0.1 g or 33%.

Under similar conditions (225°), the sodium salt of *p*-methylbenzaldehyde tosylhydrazone also gave a light-colored product (at liquid nitrogen temperatures) which turned black upon warming. Nmr analysis of the condensate showed 53% of the volatile product (corresponding to 24% yield) to be a material which, upon isolation (activity grade II alumina), was a black, noncrystalline solid with spectral properties consistent with dimethylheptafulvalene: nmr τ 8.20 (singlet with shoulder, six protons), 4.28 (structured singlet, ten protons); uv λ_{max} (EtOH) 233 $m\mu$ (ϵ 23,100); 368 (21,700). As in the case of heptafulvalene itself, the dimethyl product is too unstable (complete decomposition in air in 15 min) for elemental analysis. However, it was readily hydrogenated in ethanol (Adams catalyst) to a product that shows all properties anticipated for dimethylbicycloheptyl: mass spectrum *m/e* 222 (M), 111; nmr, complex multiplet, τ 8.0–9.2; bp 40–50° (0.05–0.07 mm). *Anal.* Calcd for $C_{16}H_{30}$: C, 86.40; H, 13.60. Found: C, 86.25; H, 13.48.

Pyrolysis of a Mixture of the Sodium Salts of Benzaldehyde and *p*-Methylbenzaldehyde Tosylhydrazones. An equimolar mixture of the two sodium salts (2.23 g) was introduced into the hot tube at 250°, at a pressure of 40 mm. The resulting mixture of heptafulvalenes was purified by chromatography on 150 g of activity grade II basic alumina (eluted with petroleum ether). The petroleum ether solution was concentrated to 30 ml and 150 ml of ether and 50 mg of PtO_2 were added. The mixture was hydrogenated at atmospheric pressure for 5 hr. The gc of the resulting mixture showed peaks corresponding to bicycloheptyl, dimethylbicycloheptyl, and a new material of intermediate retention time (ratio *ca.* 1:1:2). Isolation of the intermediate material showed a mass spectrum (*m/e* 208 (M), 111, 97) which leaves little question but that it is monomethylbicycloheptyl.

Pyrolysis of Diphenyldiazomethane. In a typical run, diphenyldiazomethane, 545 mg (2.81 mmol), was coated on 850 mg of Chromosorb P and introduced over a 10-min period to the pyrolysis column maintained at 350° (3 mm) in a stream of nitrogen (metered externally at 0.1 l./min). The volatile products were collected in a trap cooled with liquid nitrogen. The resulting beige-colored solid changed to a deep orange-brown viscous material on warming to room temperature. Chromatography of the orange residue, 452 mg, over Woelm basic alumina (75 g, activity grade II) eluting with pentane gave a white solid, mp 111–113°, with ir and nmr spectra identical with those of an authentic sample of fluorene (Sadtler[51] ir 7540, nmr 288) (lit.[52] mp 116°)). This was followed by tetraphenylethylene which could be obtained free of fluorene by several recrystallizations from ethanol–benzene, mp 223–224° (Sadtler[51] ir 20,510, nmr 2355 (lit.[53] mp 224°)). Elution with 10% ether in pentane gave a red-orange liquid which was shown to be a difficultly separable mixture of triphenylheptafulvene and diphenylheptafulvalene. Finally, using 50% ether in pentane as the eluent, benzophenone azine was isolated, mp 157–159° (lit.[54] mp 161.5°). The yields were: fluorene (29%), tetraphenylethylene (10%), triphenylheptafulvene (13%), diphenylheptafulvalene (4%), and benzophenone azine (18%).

Identification of Triphenylheptafulvene. Careful column chromatography of the red-orange liquid obtained from pyrolysis of diphenyldiazomethane with 4% ether in pentane, again over Woelm basic alumina II, allowed separation into two components. The spectra of the slower moving component were identical with those of an authentic sample of diphenylheptafulvalene (*vide infra*). The faster moving component was a red-orange viscous liquid, bp 110–120° (0.06 mm).

The ir spectrum (neat) showed absorptions at 3060, 3025, 1599, 1490, 1444, 1077, 1031, 789 (s), 760 (s), 699 (s), and 673 cm^{-1}.

The nmr[55] (CCl_4) revealed complex resonances in the aromatic region consisting of a singlet at τ 2.79 and a singlet at τ 3.15 superimposed on a complex multiplet at τ 2.80–3.15, heptafulvene resonances at τ 3.48–4.15 with a relative area ratio of 15.6:5.0. The uv spectrum in ethanol exhibited maxima at 320 $m\mu$ (ϵ 8.670) and 238 (22,000). The mass spectrum at 70 eV showed *m/e* peaks at 332 (molecular ion and base peak), 331, 244, 254, 253, 252, 241, 239, 178, 167, 165, 127, 126, 105, 77, and 51. A satisfactory analysis could not be obtained for this compound.

Ozonolysis of the orange liquid in ethanol at −78° followed by reduction of the ozonide with zinc dust in acetic acid gave a peak on vpc with the same retention time as that of benzophenone. Coinjection of a reaction sample with known benzophenone gave only one sharp peak in that region. Thin layer chromatography of the reaction residue gave a fluorescent blue band with the uv spectrum in ethanol of benzophenone. A sample of triphenylheptafulvene was recovered unchanged from pyrolysis under vacuum at 350°.

Hydrogenation of Triphenylheptafulvene. A sample of triphenylheptafulvene (53 mg) separated by careful chromatography was dissolved in absolute ethanol and reduced by hydrogenation over platinum oxide. Absorption of hydrogen reached 42 ml over a 4-hr period. The suspension was passed through a glass frit removing the platinum, and the filtrate was concentrated to a residue which showed complete loss of vinyl proton resonances in the nmr spectrum. Tlc indicated two components when developed with pentane. A preparative tlc of the residue developed with pentane was used to obtain samples of the two components. The faster-moving band (minor components) gave a molecular ion at *m/e* 344 in its mass spectrum, while that of the major, slower-moving component appeared at *m/e* 338. Lack of sample prevented analysis of the *m/e* 344 component. Sublimation of the *m/e* 338 component yielded a viscous, clear oil at 100° (0.05 mm) with the following spectral properties: ir (neat) 3080, 3060, 3025, 2915 (s), 2858, 1600, 1493, 1451, 1444, 1076, 1033, 850, 779, 756, 742, 702, 630, 597, 310, and 295 cm^{-1}; nmr (CCl_4) τ 2.7–3.2 (aromatic), 6.0–6.5 (benzylic), and other resonances at 7.2–9.1 with an area ratio of 15.0:1.3:15.1; mass spectrum (70 eV), *m/e* 338 (molecular ion and base peak), 281, 267, 205, 203, 191, 167, 165, 129, 119, 117, 115, and 91. *Anal.* Calcd for $C_{26}H_{26}$: C, 92.26; H, 7.74. Found: C, 92.22; H, 7.54.

Ozonolysis of the hydrogenation product gave two products which had glc retention times identical with those of benzophenone and 2-phenylcycloheptanone, respectively. Coinjection with authentic samples of benzophenone and 2-phenylcycloheptanone[56] gave single sharp peaks in each region.

2-Phenyltropone and 2-Phenyltropone Tosylhydrazone. 2-Phenyltropone tosylhydrazone was prepared from tropolone according to the method of Doering and Hiskey.[57] The tropolone used for this synthesis was obtained from Aldrich Chemical Co., and was carefully sublimed before use. The ir spectrum of the yellow solid, mp 80–83° (lit.[58] mp 84.5–85.5°) (68%), was identical with that reported. The tosylhydrazone was obtained as follows. A mixture of 626 mg (3.44 mmol) of 2-phenyltropone and 643 mg (3.46 mmol) of *p*-toluenesulfonylhydrazide together with 3 ml of acetic acid were refluxed in 100 ml of benzene for 17 hr. Concentration of the red solution gave a deep-red oil which was washed several times with pentane to remove any residual acetic acid. The red oil was taken up in methylene chloride and chromatographed over neutral alumina. The column was eluted with pentane, ether, methylene chloride, and finally methanol. Crystallization from methylene chloride–pentane gave 427 mg (35%) of an orange solid:

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(51) The Sadtler Standard Spectra, Sadtler Research Laboratories, Philadelphia, Pa., 1968.

(52) M. Orchin, *J. Amer. Chem. Soc.*, 67, 499 (1945).

(53) R. E. Buckles and G. M. Matlack, "Organic Syntheses," Collect. Vol. IV, Wiley, New York, N. Y., 1963, p 914.

(54) I. A. Dyakanov, *Zh. Obshch. Khim.*, 21, 1968 (1951); *Chem. Abstr.*, **46**, 6591b (1951).

(55) For nmr and uv spectra of a number of other heptafulvenes, see H. J. Dauben, Jr., and R. B. Medz, Abstracts, 145th National Meeting of the American Chemical Society, New York, N. Y., Sept 1963, p 7S: T. Nozoe, T. Mukai, A. Sato, and I. Osaka, *Bull. Chem. Soc. Jap.*, 34, 1384 (1961).

(56) We are indebted to Dr. M. A. Battiste for an authentic sample of 2-phenylcycloheptanone.

(57) W. v. E. Doering and C. F. Hiskey, *J. Amer. Chem. Soc.*, 74, 5688 (1952).

(58) E. Miller and H. Fricke, *Justus Liebigs Ann. Chem.*, **661**, 38 (1963).

mp 152–154°; ir (KBr) 3420, 3212, 2912, 1594, 1489, 1441, 1410, 1385 (broad), 1343, 1187, 1165 (s), 1095, 1049, 1019, 932, 880, 816, 771, 755, 700, 674, 573, and 554 cm^{-1}; nmr ($CDCl_3$) singlets at τ 2.63 and 2.77 (total area, 10), 3.39–3.74 (complex multiplet, 4.5), 7.61 (s, 3.3); uv (ethanol) λ 314 nm (ϵ 8820) and 223 (22,300). *Anal.* Calcd for $C_{20}H_{18}N_2O_2S$: C, 68.56; H, 5.18; N, 8.00. Found: C, 68.81; H, 5.45; N, 7.80.

Solution Pyrolysis of the Sodium Salt of 2-Phenyltropone Tosylhydrazone. Isolation of 2,2′-Diphenylheptafulvalene. To a solution of 180 mg (0.51 mmol) of 2-phenyltropone tosylhydrazone in 50 ml of dry tetrahydrofuran was added slowly 35 mg (1.46 mmol) of sodium hydride (pentane washed). The red solution rapidly darkened with vigorous bubbling. After stirring for 20 min, the mixture was concentrated to a red-brown paste, which was taken up in 3 ml of diglyme (freshly distilled from $LiAlH_4$). The salt solution was added dropwise from a syringe to 50 ml of diglyme previously heated to 100° under a gas buret. Total nitrogen evolution over a 20 min period was greater than 80% of theoretical. Uv analysis of an aliquot in ethanol showed an 86% yield. The orange solution was decanted and the residue washed twice with ether and filtered. The filtrate was treated with 150 ml of water, and the aqueous layer washed with three 50-ml portions of ether. The ether extracts were combined and washed with six 25-ml portions of water to remove most of the diglyme, then dried over $MgSO_4$. Concentration gave a red-orange slurry, which was taken up in pentane–ether and chromatographed over Woelm basic alumina (activity grade II). Elution with 4% ether in pentane gave a red solid: mp 137–142°; ir spectrum (melt) 3020, 2970, 2910, 1550, 1455, 1445, 1390, 1185, 1080, 1035, 910, 875, 868, 778, 753 (s), 726 (s), 713 (s), and 690 (s) cm^{-1}; nmr ($CDCl_3$) aromatic singlet at 2.99 superimposed on a complex multiplet at τ 2.50–3.31 and heptafulvalene resonances at 3.32–4.39, relative area ratio 10.2:10.0; uv (ethanol) 319 mμ (ϵ 13,540), and 245 (17,080); mass spectrum (70 eV) *m/e* 333 (M + 1), 332 (molecular ion), 255, 254, 253, 241, 239, 179, 178 (base peak), 166, 165, 57, and 55. *Anal.* Calcd for $C_{26}H_{20}$: C, 93.94; H, 6.06. Found: C, 93.70; H, 6.36.

A sample of diphenylheptafulvalene was unstable to vacuum pyrolysis at 350°, but neither fluorene nor triphenylheptafulvene was formed.

Hot-Tube Pyrolysis of 4-Methyldiphenyldiazomethane and 4-Methoxydiphenyldiazomethane. In a typical run, 590 mg (2.84 mmol) of 4-methyldiphenyldiazomethane was coated on 2.0 g of Chromosorb P. The solid deposit was pyrolyzed at 355° (4 mm) in the described manner with a total addition time of 10–12 min (0.1 l./min nitrogen flow). The crude yellow-orange liquid was taken up in pentane and chromatographed over 100 g of basic alumina II. Elution with pentane gave 150 mg (29%) of a white solid, mp 101–102° (lit.[59] 104°). The ir and nmr spectra were identical with known 2-methylfluorene (Sadtler[51] ir 19,968, nmr 4307). Further chromatography gave a red-orange liquid which was not fully characterized. The crude 2-methylfluorene was analyzed for 3-methylfluorene as follows. A mixture of 4.4% 3-methylfluorene and 95.6% crude 2-methylfluorene from the pyrolysis when introduced onto a 10% Apiezon L capillary gc column at 180° showed two well-resolved peaks. Similar injection of the crude 2-methylfluorene showed no trace of the 3 isomer. 4-Methoxydiphenyldiazomethane was pyrolyzed in the same way and found to give, after chromatography on basic alumina (activity grade II), 2-methoxyfluorene (12%), mp 105–108° (lit.[60] mp 109°).

Hot-Tube Pyrolysis of the Sodium Salt of 2-Phenyltropone Tosylhydrazone. Treatment of 171 mg (0.49 mmol) of 2-phenyltropone tosylhydrazone with an equivalent of sodium hydride in dry THF at room temperature generated a vigorous exothermic reaction with subsequent darkening to a brown solution. Addition of 1.5 g of Chromosorb P and removal of the solvent under reduced pressure resulted in a dark-brown solid suitable for pyrolysis. The salt was pyrolyzed at 340° (4 mm) under a stream of nitrogen (0.1 l./min). The dark yellow-green pyrolysate was separated on preparative tlc developing with pentane into three components. The first component was fluorescent under uv light and collection of the material gave fluorene in 15% yield. It was identified by comparison of its nmr spectrum with that of an authentic sample, by glc retention time, and by coinjection with an authentic sample of fluorene which gave a single, sharp peak. The second component was a yellow band obtained in 50% yield. Its nmr spectrum was very similar to that of diphenylheptafulvalene. The uv spectrum exhibited maxima at 320 and 240 mμ. The mass spectrum (70 eV) showed a molecuar ion at *m/e* 332 and other peaks at 255, 244, 253, 252, 241, 205, 178, 167, 165, 119, 117 (base peak), 57, 43, and 41. The third component was not identified.

4-Methyltropone Tosylhydrazone. 4-Methyltropone was synthesized from *p*-methylanisole by expansion with methylene[61] followed by oxidation with bromine.[61] Its tosylhydrazone was synthesized in the conventional way.[62] For complete details of this synthesis, see the M.S. thesis of Terry L. Davis, University of Florida, June, 1971.

2-Methyltropone Tosylhydrazone. A solution of 982 mg (8.4 mmol) of freshly sublimed tropolone in 30 ml of anhydrous ether was added rapidly from a dropping funnel to 65 ml of a 5.1% methyllithium in ether solution at 0° (density 0.71 g/ml) (107 mmol). The reaction was vigorous. After stirring at room temperature for 40 min, 35 ml of 3 *N* H_2SO_4 was dripped in very slowly. The ether layer was separated and washed with two 30-ml portions of water. The ether extracts were dried over $MgSO_4$ and concentrated to a dark green oil which appeared to rapidly decompose.

The crude tropone mixture was, therefore, immediately taken up in 100 ml of absolute ethanol along with 4 ml of concentrated HCl and 1.51 g (8.1 mmol) of *p*-toluenesulfonylhydrazide and refluxed for 15 min. The mixture had darkened in color, so refluxing was discontinued, and the excess ethanol was removed under reduced pressure. The liquid residue was treated with 100 ml of water and extracted with three 50-ml portions of methylene chloride. The methylene chloride residue was chromatographed over 50 g of silica gel collecting the red-orange fraction which was eluted with 15–20% ether in hexane. Concentration yielded a red-orange solid, 150 ml (6.5%), which showed an nmr consistent with 2-methyltropone tosylhydrazone: A_2B_2 pattern with doublets centered at τ 2.13 (J = 8 cps) and 2.77 (J = 8 cps), tropone resonances at τ 3.52–3.91, a methyl singlet at τ 7.61 and another methyl singlet at τ 7.95. The relative area ratios of aromatic to tropone to methyl to methyl were 3.9:4.6:3.0:3.1, respectively. The ir spectrum revealed an absorption at 1160 cm^{-1} which is typical of tosylhydrazones, and no carbonyl absorption was observed. The solid could not be induced to crystallize and an acceptable analysis was not obtained.

Pyrolysis of the Sodium Salts of 2- and 4-Methyltropone Tosylhydrazone. The sodium salts, prepared in the conventional way, were pyrolyzed at 350° (3 mm, 0.1 l./min) and 450° (6 mm, 0.21 l./min), respectively. Nmr and gc analysis of the condensates showed only styrene from the 2-methyl isomer and equal amounts of styrene and benzocyclobutene from the 4-methyl isomer.

Photolysis of *o*-, *m*-, and *p*-Tolyldiazomethane. The appropriate tolyldiazomethane (*ca.* 0.1 g) was placed in a small flask which was attached to the flow photolysis apparatus which consisted of (in series) a sublimation flask, a Pyrex or quartz photolysis region, a liquid nitrogen trap, and a vacuum pump. The flask was cooled to 0° and the pressure was lowered to 2 mm. Under these conditions, the tolyldiazomethane slowly sublimed through the photolysis region of the apparatus which employed a Hanovia 550-W medium-pressure mercury lamp. Five to nine hours were required. The products were collected in the liquid nitrogen trap. The photolysate (mostly starting material) was taken up in CCl_4–TMS. The ratio of benzocyclobutene to styrene was determined by nmr analysis using the singlet at 6.88 ppm and the multiplet at 5.4 ppm, respectively. These data are listed in Table I. Control experiments without irradiation showed that benzocyclobutene and styrene were not present in the starting tolyldiazomethanes in detectable amounts.

Pyrolysis of the Sodium Salt of Benzaldehyde Tosylhydrazone in Diglyme. To 30 ml of dry diglyme in a 3-oz Fischer–Porter aerosol compatibility tube was added 0.10 g (0.34 mmol) of the sodium salt of benzaldehyde tosylhydrazone. The sealed tube was placed in an oil bath preheated to 165° for 30 min. At the end of this time all trace of color of the diazo was gone, leaving the solution colorless. The mixture was allowed to cool, poured into water (200 ml), and extracted with pentane (three 30-ml portions). The combined pentane extracts were washed with water (three 50-ml portions), dried ($MgSO_4$), and concentrated on a rotary evaporator. The nmr spectrum of the residue, a light-yellow oil, indicated no hepta-

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(59) O. Kruber, *Chem. Ber.*, 65, 1382 (1932).

(60) G. W. Gray, J. B. Hartley, and A. Ibbotson, *J. Chem. Soc.*, 2686 (1955).

(61) *Cf.* E. Miller and H. Fricke, *Justus Liebigs Ann. Chem.*, **661**, 38 (1963); H. R. Snyder and Z. Wicks, Jr., in "Organic Syntheses," Collect. Vol. III, E. C. Horning, Ed., Wiley, New York, N. Y., 1959, pp 15–21; W. von E. Doering and F. L. Detert, *J. Amer. Chem. Soc.*, 73, 876 (1951).

(62) W. M. Jones and C. L. Ennis, *ibid.*, **91**, 6391 (1969).

fulvalene was present, only what is believed to be the phenylcarbene–diglyme adducts. In addition, there was aldazine produced in the reaction. Comparative tlc of the residue confirmed the absence of heptafulvalene.

Pyrolysis of the Sodium Salt of Tropone Tosylhydrazone in Diglyme. Into a Carius tube was placed 80 mg (0.27 mmol) of the sodium salt of tropone tosylhydrazone and 10 ml of dry diglyme. The sealed tube was immersed in an oil bath preheated to 210° and allowed to remain for 30 min. Upon cooling, the tube was opened and the contents poured into water (120 ml) and extracted with pentane (three 35-ml portions). The combined pentane extracts were washed with water (three 50-ml portions) and dried ($MgSO_4$). The dry pentane solution was concentrated on a rotary evaporator to yield a very dark solid. The nmr spectrum of the residue was identical with that of heptafulvalene with a small amount of aromatic resonance but none at the position expected for phenylcarbene–diglyme insertion products.

4,5-Benzotropone Tosylhydrazone. In a typical run, 2.00 g (0.013 mol) of 4,5-benzotropone,[63] 2.38 g (0.013 mol) of *p*-toluenesulfonylhydrazide, and 2 drops of concentrated sulfuric acid were placed in 55 ml of 95% ethyl alcohol and heated at reflux for 1 hr. Upon cooling, 4,5-benzotropone tosylhydrazone precipitated from the solution and was isolated by filtration. Recrystallization from absolute ethyl alcohol yielded 2.15 g (51%) of the product. There were two crystal forms of the tosylhydrazone: red plates (mp 186–189°); and yellow needles (mp 180–185°). The other properties of the tosylhydrazone were as follows: ir (KBr) 3200, 1638, 1325, 1165, 575, 555 cm^{-1}; nmr (acetone-d_6) τ 2.00–2.80 (A_2B_2, 4 H, J = 8 cps, toluoyl aromatic), 2.62 (s, 4 H, benzo), 2.90–3.80 (m, 4 H, cycloheptatrienyl), 7.60 (s, 3 H, methyl); mass spectrum 324 (M^+). *Anal.* Calcd for $C_{18}H_{16}N_2O_2S$: C, 66.64; H, 4.97; N, 8.64; S, 9.89. Found: C, 66.52; H, 5.07; N, 8.57; S, 9.97

Pyrolysis of the Sodium Salt of 4,5-Benzotropone Tosylhydrazone in Benzene. To a 3-oz Fischer–Porter aerosol compatibility tube containing 35 ml of benzene was added 0.20 g (0.58 mmol) of the sodium salt of 4,5-benzotropone tosylhydrazone. The sealed tube was placed in an oil bath preheated to 120° and allowed to remain for 2.5 hr. The color of the reaction mixture changed from orange to light yellow during the course of the reaction. Upon cooling, the nitrogen evolution was monitored and 81% of the theoretical amount had evolved. The reaction mixture was filtered and the residue was washed with ethyl ether. The total filtrate was concentrated on a rotary evaporator to give 122 mg (96%) of crude 2-(2,4,6-cycloheptatrien-1-yl)naphthalene.[64] Recrystallization from absolute methyl alcohol yielded 68 mg (54%) of yellow crystals, mp 85–86° (sublimation at 90° and 0.1 mm Hg gave white plates with same mp): ir (KBr) 3060, 3020, 1600, 1500, 1280, 1260, 950, 900, 860, 820, 745, 700, 480 cm^{-1}; nmr ($CDCl_3$) τ 2.10–2.70 (m, 7 H, naphthyl), 3.26 (broad t, 2 H, 4 and 5 cycloheptatrienyl), 3.55–3.90 (complex m, 3 H, 3 and 6 cycloheptatrienyl), 4.33–4.70 (m, 2 H, 2 and 7 cycloheptatrienyl), 7.10 (m, 1 H, methine); mass spectrum 218 (M^+). *Anal.* Calcd for $C_{17}H_{14}$: C, 93.54; H, 6.46. Found: C, 93.39; H, 6.48.

The sodium salt of β-naphthaldehyde tosylhydrazone was pyrolyzed and worked-up in a manner analogous to the one above to yield 78% 2-(2,4,6-cycloheptatrien-1-yl)naphthalene and 6% of the aldazine.

Photolysis of the Sodium Salt of 4,5-Benzotropone Tosylhydrazone in Benzene. To 60 ml of benzene in a photolysis vessel which consisted of a Pyrex tube with a side arm and equipped with a small mechanical stirrer, was added 0.10 g (0.29 mmol) of the sodium salt of 4,5-benzotropone tosylhydrazone. The mixture was rapidly stirred and the photolysis carried out by mounting the apparatus vertically alongside and as close as possible to a 550-W Hanovia medium-pressure mercury lamp in a Pyrex tube. Both the vessel and the tube containing the lamp were immersed in a circulating water bath which kept the temperature at 30°. The salt was photolyzed for 30 min with 84% of the theoretical amount of nitrogen being evolved as monitored by a gas buret fitted to the side arm of the photolysis vessel. The reaction mixture was filtered and the residue was washed with ethyl ether. The total filtrate was concentrated on a rotary evaporator to yield 37 mg (59%) of 2-(2,4,6-cycloheptatrien-1-yl)naphthalene which had all the properties of the pyrolysis product.

The sodium salt of β-naphthaldehyde tosylhydrazone was photolyzed in a manner analogous to the above salt to yield 67% of 2-(2,4,6-cycloheptatrien-1-yl)naphthalene.

Pyrolysis of the Sodium Salt of 4,5-Benzotropone Tosylhydrazone in Cyclohexane. In a 3-oz Fischer–Porter aerosol compatibility tube containing 20 ml of cyclohexane was placed 0.40 g (1.1 mmol) of the sodium salt of 4,5-benzotropone tosylhydrazone. The sealed tube was placed in an oil bath which was preheated to 115° and allowed to remain for 1.25 hr. Nitrogen evolution was 100% of the theoretical amount. The reaction mixture was allowed to cool and then filtered. The residue was washed with ethyl ether and the total filtrate concentrated on a rotary evaporator. The remaining yellow oil was chromatographed on alumina, eluted with pentane, yielding 131 mg (51%) of (β-naphthyl)cyclohexylmethane. The nmr spectrum of the crude material indicated almost exclusive adduct and cyclohexane. An analytical sample of the compound was purified by preparative vpc (18 ft × 0.25 in. 20% SE-30 on Chromosorb W at 222°) retention time 32 min and had the following properties: ir (film) 3042, 3010, 2920, 2845, 1601, 1445, 815, 795 cm^{-1}; nmr ($CDCl_3$) τ 2.10–2.90 (m, 7 H, naphthyl), 7.35 (d, 2 H, J = 7 cps, benzylic), 8.10–9.20 (m, 11 H, cyclohexyl); mass spectrum 225 (M^+), 141 ($C_{11}H_9$), 83 (C_6H_{11}).

Reaction of the Sodium Salt of β-Naphthaldehyde Tosylhydrazone with Dimethyl Fumarate at 105°. To a 3-oz Fischer–Porter aerosol compatibility tube containing 20 ml of benzene was added 0.20 g (0.58 mmol) of the sodium salt of β-naphthaldehyde tosylhydrazone and 83 mg (0.58 mmol) of dimethyl fumarate (previously washed with saturated aqueous sodium bicarbonate and recrystallized from chloroform). The sealed tube was placed in an oil bath preheated to 105° and was allowed to remain there for 5 hr. Upon cooling, the reaction mixture was filtered. The residue was washed with ethyl ether and the total filtrate was concentrated on a rotary evaporator yielding 90 mg (50%) of an almost colorless, very viscous oil. The oil was not stable to ordinary distillation conditions and even though column chromatography on silica gel effected some purification, it was not sufficient to provide a sample which gave a good elemental analysis (*e.g.*, 8.97% N (calcd); 8.31% (found)). The other physical data were all consistent with the 3,4-dicarbomethoxy-5-naphthyl-2-pyrazoline structure: ir (film) 3440 (N–H), 3050, 2945, 1730 (unconjugated ester carbonyl), 1700 (conjugated ester carbonyl), 1555 (C=N), 1440, 1200, 1015, 855, 815, and 750 cm^{-1}; nmr ($CDCl_3$) τ 2.10–2.60 (m, 7 H, naphthyl), 3.24 (broad s, 1 H, nitrogen), 4.60 (broad d, 1 H, J = 9 cps, benzylic), 5.92 (d, 1 H, J = 9 cps, α-carbomethoxy), 6.18 (s, 3 H, conjugated ester methyl), 6.24 (s, 3 H, unconjugated ester methyl); mass spectrum no (M^+), 284 (M^+ − 28); uv (95% C_2H_5OH) 224 mμ (log ϵ 4.53), 275 (3.75), 287 (3.79).

Reaction of the Sodium Salt of 4,5-Benzotropone Tosylhydrazone with Dimethyl Fumarate. Into a 3-oz Fischer–Porter aerosol compatibility tube containing 20 ml of benzene were placed 0.20 g (0.58 mmol) of the sodium salt of 4,5-benzotropone tosylhydrazone and 83 mg (0.58 mmol) of dimethyl fumarate (previously washed with saturated aqueous sodium bicarbonate and then recrystallized from chloroform). The sealed tube was placed in an oil bath preheated to 105° and allowed to remain for 5 hr. Upon cooling, the mixture was filtered. The residue was washed with ethyl ether and the total filtrate concentrated on a rotary evaporator to yield 76 mg (63%) of 2-(2,4,6-cycloheptatrien-1-yl)naphthalene. Comparative tlc on silica gel eluted with 50:50 ethyl ether–pentane of the known pyrazoline and this reaction mixture indicated no pyrazoline was present in the latter.

Hot-Tube Pyrolysis of Sodium Salts of Methylnaphthaldehyde Tosylhydrazones. The tosylhydrazone salts were pyrolyzed in the usual manner at temperatures recorded in Table II. The pressure was always set at 5 mm. After the pyrolysis was completed, both the pyrolysis tube and the trap were washed with CCl_4 to give a total volume of 100 ml. The washings were dried with Na_2SO_4 and 1 ml (or 2 ml) of CCl_4 solution of dibenzyl ether (0.1874 mol/l., internal standard) was added with a pipet. The solvent was then removed and the residue was dissolved in $CDCl_3$ for analysis by nmr. $CDCl_3$ was then removed and the residue or its *n*-pentane extract was dissolved in benzene for analysis by glc. Solutions of both of the naphthocyclobutenes and both of the vinylnaphthalenes were carefully calibrated with known materials obtained as follows. 1-Vinylnaphthalene was prepared according to the method of Buu-Hoi and Lecoq.[65] Commercially available 2-vinylnaphthalene (recrystallized from ethanol), mp 66°, was used. Naphtho[*b*]cyclobutene was prepared by the method of Cava[66] and naphtho[*a*]cyclobutene was isolated directly from pyrolysis of the sodium

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[63] J. Thiele and E. Weitz, *Justus Liebigs Ann. Chem.*, **377**, 1 (1910).

[64] C. Jutz and F. Voithenleitner, *Chem. Ber.*, **97**, 29 (1964).

[65] N. P. Buu-Hoi and J. Lecoq, *J. Chem. Soc.*, 830 (1946).

[66] M. P. Cava and R. L. Shirley, *J. Amer. Chem. Soc.*, **82**, 654 (1960).

salts of 2-methyl-1-naphthaldehyde tosylhydrazone and identified by its mass spectrum (*m/e* 154 (M)) and comparison of its rather structured uv with that of the known material.[67]

2-Methyl-4,5-benzotropone Tosylhydrazone. In a typical run, 2.00 g (0.012 mol) of 2-methyl-4,5-benzotropone, 2.18 g (0.012 mol) of *p*-toluenesulfonylhydrazide, and 5 drops of concentrated sulfuric acid were placed in 40 ml of absolute ethyl alcohol and heated at reflux for 1 hr. Upon cooling, 2-methyl-4,5-benzotropone tosylhydrazone precipitated from solution and was isolated by filtration. Recrystallization from absolute ethyl alcohol yielded 2.4 g (60%) of the product as yellow-gold plates, mp 182–184°: ir (KBr) 3180, 1630, 1590, 1555, 1420, 1385, 1330, 1165, 1022, 915, 805, 760, 680, and 580 cm^{-1}; nmr (CDCl$_3$) τ 2.00–3.00 (A_2B_2, 4 H, J = 8 cps, aromatic), 2.78 (s, 4 H, benzo), 3.05–3.70 (m, 3 H, cycloheptatrienyl), 7.62 (s, 3 H, *p*-methyl), 7.88 (d, 3 H, cycloheptatrienyl methyl); mass spectrum 339 (M$^+$). *Anal.* Calcd for $C_{19}H_{18}N_2O_2S$: C, 67.43; H, 5.36; N, 8.28. Found: C, 67.39; H, 5.33; N, 8.40.

Pyrolysis of the Sodium Salt of 2-Methyl-4,5-benzotropone Tosylhydrazone in Benzene. To a Fischer–Porter aerosol compatibility tube containing 35 ml of benzene was added 216 mg (0.60 mmol) of the sodium salt of 2-methyl-4,5-benzotropone tosylhydrazone. The sealed tube was placed in an oil bath preheated to 130° for 20 min. By the end of this time the yellow mixture had changed to a very light yellow-green. The mixture was allowed to cool and filtered. The residue was washed with ethyl ether and the total filtrate concentrated on a rotary evaporator to yield 80 mg of products. Analysis of the product mixture by nmr indicated the presence of 2-vinylnaphthalene and 2-(2,4,6-cycloheptatrien-1-yl)-3-methylnaphthalene (comparisons were made using commercially available 2-vinylnaphthalene from Aldrich Chemical Co. and 2-(2,4,6-cycloheptatrien-1-yl)-3-methylnaphthalene from the pyrolysis of the sodium salt of the tosylhydrazone of 2-methyl-3-naphthaldehyde in benzene). Analysis by vpc (3 ft × 0.25 in. 15% SE-30 on Chromosorb W at 190°) indicated three products in the reaction mixture (the known ones were established by comparison with known samples): (1) retention time 1 min, 2-vinylnaphthalene (72%); (2) retention time 10 min, unknown compound (6%); (3) retention time 14 min, 2-(2,4,6-cycloheptatrien-1-yl)-3-methylnaphthalene (22%). Products 1 and 3 were isolated in 44% and 20% overall yield, respectively. 2-(2,4,6-Cycloheptatrien-1-yl)-3-methylnaphthalene (sublimed at 90° and 0.1 mm) had the following properties: mp 65–68°; ir (KBr) 3055, 3010, 1600, 1500, 1440, 1220, 1010, 890, 745, 700, and 480 cm^{-1}; nmr (CDCl$_3$) τ 2.00–2.90 (m, 6 H, naphthyl), 3.25 (broad s, 2 H, 4 and 5 cycloheptatrienyl), 3.50–3.90 (complex pattern, 2 H, 3 and 6 cycloheptatrienyl), 4.35–4.76 (complex pattern, 2 H, 2 and 7 cycloheptatrienyl), 6.95 (broad t, 1 H, methine), 7.65 (s, 3 H, methyl); mass spectrum 232 (M$^+$). *Anal.* Calcd for $C_{18}H_{16}$: C, 93.06; H, 6.94. Found: C, 92.85; H, 7.00.

The sodium salt of 3-methyl-2-naphthaldehyde tosylhydrazone was pyrolyzed in the same manner as the above salt except that 40 ml of benzene was used and the temperature was 145°. The products were aldazine (42%) and 2-(2,4,6-cycloheptatrien-1-yl)-3-methylnaphthalene (39%).

Acknowledgment. The authors are indebted to the National Science Foundation and to the Petroleum Research Fund, administered by the American Chemical Society, for their generous support of this research.

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Recovery of *R* Allenes from the Partial Hydroboration of Racemic Allenes with (+)-Tetra-3-pinanyldiborane. A Model for Hydroboration of Olefins and Allenes[1]

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Abstract: A series of racemic allenes was partially hydroborated with (+)-tetra-3-pinanyldiborane derived from (−)-α-pinene. In every case the recovered allene was enriched in the *R* enantiomer. Where necessary, absolute configurations were assigned by reference to allene sector rules in conjunction with ORD–CD measurements. Optical purities appeared to increase in the order 1,3-dimethylallene < 1,2-cyclononadiene < 1,3-di-*tert*-butylallene < 1,3-diethylallene < 1,3-di-*n*-propylallene. Hydroboration of both 1,3-di-*tert*-butylallene and 1,3-diethylallene with both fresh and aged tri- and di-3-pinanyldiborane reagents gave recovered allene having a lower optical purity but still the *R* configuration. The regiospecificity, *ca.* 70% vinyl- and 30% allylborane formation (determined for 1,2-cyclononadiene), paralleled that found previously for other reagents. An analysis of prior data and models for hydroboration of olefins has led to the proposal of a model for asymmetric hydroboration with tetra-3-pinanyldiborane. This model, which uses a simple shape for the reagent and allows nonplanarity of a four-center transition state, correctly predicts the stereochemistry of hydroboration of allenes.

Over a decade ago, Brown and his coworkers introduced the use of optically active alkylboranes as hydroborating agents which could effect the transformation of an appropriate olefin into an optically active alcohol.[2] At the same time, Brown showed that from the partial hydroboration of a chiral olefin it was possible to achieve a "kinetic resolution" leading to the recovery of an optically active olefin.[2b,3] To date, the most useful reagent has proved to be the first one reported by Brown, *viz.*, tetra-3-pinanyldiborane, hereafter referred to as $Pn_4B_2H_2$ or $Pn_2BH_2BPn_2$.[4]

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[1] Acknowledgment is made to the National Science Foundation for support of this research (GP 25216).

[2] (a) H. C. Brown and G. Zweifel, *J. Amer. Chem. Soc.*, **83**, 486 (1961); (b) H. C. Brown, N. R. Ayyangar, and G. Zweifel, *ibid.*, **86**, 397 (1964).

[3] H. C. Brown, N. Ayyangar, and G. Zweifel, *ibid.*, **86**, 4341 (1964).

[4] The *Chemical Abstracts* name for this reagent is tetra-3-pinanyldiborane although it commonly has been referred to as tetraisopinocampheyldiborane. Similarly di-3-pinanylborane has been called diisopinocampheylborane. We will follow the recommendation[5] that the less cumbersome *Chemical Abstracts* nomenclature be used.

[5] J. D. Morrison and H. S. Mosher, "Asymmetric Organic Reactions," Prentice-Hall, Englewood Cliffs, N. J., 1971, p 220 ff.