Evidence for Cyclopropene Intermediates in the Rearrangement of Aromatic Carbenes to Arylcarbenes

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Abstract: A convenient, high-yield synthesis of 5*H*-dibenzo[*a,c*]cyclohepten-5-one is reported and the properties of dibenzo[*a,c*]cycloheptatrienylidene are examined. As previously reported[2] for 4,5-benzocycloheptatrienylidene, dibenzo[*a,c*]cycloheptatrienylidene rearranges rapidly in solution to an arylcarbene (9-phenanthrylcarbene). When the annelated cycloheptatrienylidenes were generated in the presence of dienes, Diels–Alder adducts of the cyclopropene intermediates were obtained. The molecular geometry of the single furan adduct of dibenzo[*a,c*]cycloheptatrienylidene was determined from an analysis of lanthanide-induced proton nmr shifts. The geometry of the adducts of both of the carbenes with cyclopentadiene is shown to be the endo-anti isomers. These are the products expected from cycloaddition of 3-monosubstituted cyclopropenes with this diene. The furan adduct was obtained under both thermal (125°) and photochemical (30 and −60°) conditions. Tetracyclone adducts were obtained in thermal reactions and cyclopentadiene and butadiene adducts were obtained from low-temperature (−60°) reactions. The adducts were shown not to be secondary photoproducts, and a two-step thermal process has been ruled out. Also, irreversible cyclopropene formation competitive with rearrangement is shown to be an unsatisfactory explanation of the experimental results.

Unlike other reactive intermediates which are highly susceptible to rearrangement, carbenes generally undergo intra- or intermolecular abstraction, insertion, or addition reactions rather than conversion to isomeric carbenes of greater stability. The interconversion of aromatic and arylcarbenes is a notable exception to this generality. Besides detailed studies concerned with the conversion of phenylcarbene (5) and its derivatives to cycloheptatrienylidenes (1) in the gas phase[1] and of benzocycloheptatrienylidene (20) to naphthylcarbene (26) in solution,[1,2] a growing number of heterocyclic[3,4] and nonbenzenoid[5,6] carbenes have been shown to undergo a similar isomerization. Yet the mechanism of this reorganization remains a subject of considerable conjecture.[7-11] Three suggested mechanistic alternatives are collected in Figure 1.

The first possibility involves a bicycloheptatriene intermediate (2) and certainly has ample precedence in the well known formation of cyclopropenes from vinyl carbenes.[12] For this reason, it is not surprising that this has been the *a priori* choice of many workers in this field. Furthermore, indirect evidence that favors this
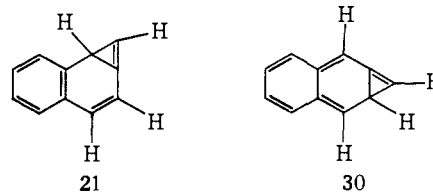
mechanism over the second possibility (the so-called Wolff mechanism) has appeared.[6,11] This evidence consisted of the observation that rearrangement occurs less readily in systems in which more highly strained fused cyclopropanes must be postulated and that the rearrangement of methyl-substituted 2-naphthylcarbenes occurs with cleavage of the 1,2 bond (the bond of higher π-bond order) to the exclusion of the 2,3 bond. It was argued that this preference would be expected of a cyclopropene mechanism whereas the opposite would

26
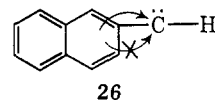
be preferred by a Wolff-type mechanism.[13] This result has recently been interpreted in terms of the relative stabilities of the two carbenes 20 and 29 rather than the degree of π-bond order of the bond into which the carbene inserts. Without doubt, intermediate stability, insofar as it reflects transition state stability, controls the bond that migrates in a carbene–carbene rearrangement. However, the intermediates that should be compared are not the carbenes 20 and 29. Instead,
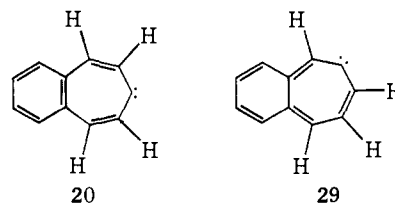
it seems better to compare for one mechanism the cyclopropenes 21 *vs.* 30, the latter being the less fav-

(1) W. M. Jones, R. C. Joines, J. A. Myers, T. Mitsuhashi, K. E. Krajca, E. E. Waali, T. L. Davis, and A. B. Turner, *J. Amer. Chem. Soc.*, **95**, 826 (1973), and references cited therein.

(2) K. E. Krajca, T. Mitsuhashi, and W. M. Jones, *J. Amer. Chem. Soc.*, **94**, 3661 (1972).

(3) W. D. Crow and C. Wentrup, *Tetrahedron Lett.*, 6149 (1968); W. D. Crow, M. N. Padden-Row, and D. S. Sutherland, *ibid.*, 2239 (1972).

(4) C. Wentrup, C. Mayor, and R. Gleiter, *Helv. Chim. Acta*, **55**, 2628 (1972).

(5) P. H. Gebert, R. A. LaBar, and W. M. Jones, *J. Amer. Chem. Soc.*, **95**, 2357 (1973).

(6) T. T. Coburn and W. M. Jones, *Tetrahedron Lett.*, 3903 (1973).

(7) G. G. Vander Stouw, A. R. Kraska, and H. Shechter, *J. Amer. Chem. Soc.*, **94**, 1655 (1972).

(8) R. C. Joines, A. B. Turner, and W. M. Jones, *J. Amer. Chem. Soc.*, **91**, 7754 (1969); J. A. Myers, R. C. Joines, and W. M. Jones, *ibid.*, **92**, 4740 (1970).

(9) W. J. Baron, M. Jones, Jr., and P. P. Gaspar, *J. Amer. Chem. Soc.*, **92**, 4739 (1970).

(10) P. O. Schissel, M. E. Kent, M. J. McAdoo, and E. Hedaya, *J. Amer. Chem. Soc.*, **92**, 2147 (1970); E. Hedaya and M. E. Kent, *ibid.*, **93**, 3285 (1971).

(11) T. Mitsuhashi and W. M. Jones, *J. Amer. Chem. Soc.*, **94**, 677 (1972).

(12) W. Kirmse, "Carbene Chemistry," 2nd ed, Academic Press, New York, N. Y., 1971, pp 328–332, and references cited therein.

(13) Also see C. Wentrup, C. Theta, and R. Gleiter, *Helv. Chim. Acta*, **55**, 2633 (1972). We thank Professor Wentrup for preprints of these papers.

ored. On the other hand, the intermediates (or transition states) that must be compared for the Wolff mechanism for didactic purposes applied to the same naphthylcarbene system, are the zwitterions **31** and **32**, with **32** the more stable.[14]

31   32
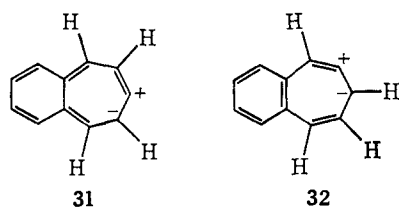
Thus, a restatement of the initial argument would be that in the case of arylcarbenes of polycyclic aromatic hydrocarbons, the more stable cyclopropene will be formed by intramolecular addition of the carbene to the bond of higher double-bond order. On the other hand, were a Wolff mechanism to pertain, the more stable zwitterion from migration of the bond of lower order would be favored.

The third mechanism in Figure 1 involving ring-opened diradicals (**4**) (or charge separated species) has also been mentioned.[1,11,15] However, this possibility appears unlikely in many systems, primarily due to the low temperatures at which some rearrangements occur,[1,2,5] the absence of hydrogen abstraction or other radical products when the rearrangement is carried out in ether solvents,[1,2] and the dramatic acceleration of the reorganization upon annelation.[1,2] The effect of annelation also argues against other mechanistic possibilities that require initial isomerization of the cycloheptatrienylidene to a norcaradienylidene.

Thus, although the available indirect evidence supports the cyclopropene mechanism, the need for direct evidence pertaining to the mechanistic question is clear. With the observation of high-yield rearrangements that occur in solution[1,2,5] experiments aimed at trapping an intermediate were undertaken. In this paper, we report the results of our attempts to trap cyclopropenes in reactions involving isomerizations of aromatic carbenes to arylcarbenes.

Results

Rearrangements of both mono- and dibenzocycloheptatrienylidene[16] (**20** and **14**) were studied. The cycloheptatrienylidenes were generated in each case from the tosylhydrazone salts which were in turn synthesized from the corresponding ketones. Synthesis of 5H-dibenzo[a,c]cyclohepten-5-one (**11**) (required for generation of **14** by previously reported[18,19] methods)

(14) (a) This type of intermediate might be even better represented by a bent and twisted allene structure. Interestingly enough, whereas recent INDO calculations[6] agree with Wentrup's conclusions that **20** should be more stable than **29**, exactly the opposite is true for the allene structures with the allene form of **29** dramatically more stable than the corresponding form of **20**. (b) For INDO calculations comparing energies of cycloheptatrienylidenes and cycloheptatetraenes, see L. Tyner, W. M. Jones, N. Y. Ohrn, and J. Sabin, *J. Amer. Chem. Soc.*, **96**, 3765 (1974).

(15) C. Wentrup, *Tetrahedron*, **26**, 4965 (1970); C. Wentrup, *ibid.*, **27**, 367 (1971).

(16) Although dibenzo[a,d]cycloheptatrienylidene has been previously studied and found to behave as a diarylcarbene with no tendency to rearrange in solution,[17] dibenzo[a,c]cycloheptatrienylidene (**14**) has not previously been reported.

(17) S.-I. Murahashi, I. Moritani, and M. Nishino, *J. Amer. Chem. Soc.*, **89**, 1257 (1967); S.-I. Murahashi, I. Moritani, and M. Nishino, *Tetrahedron*, **27**, 5131 (1971).
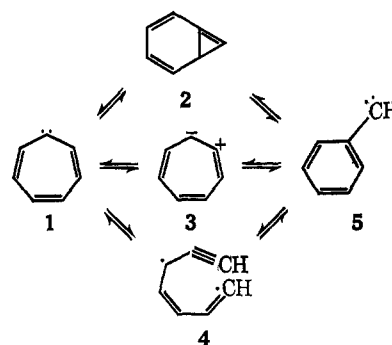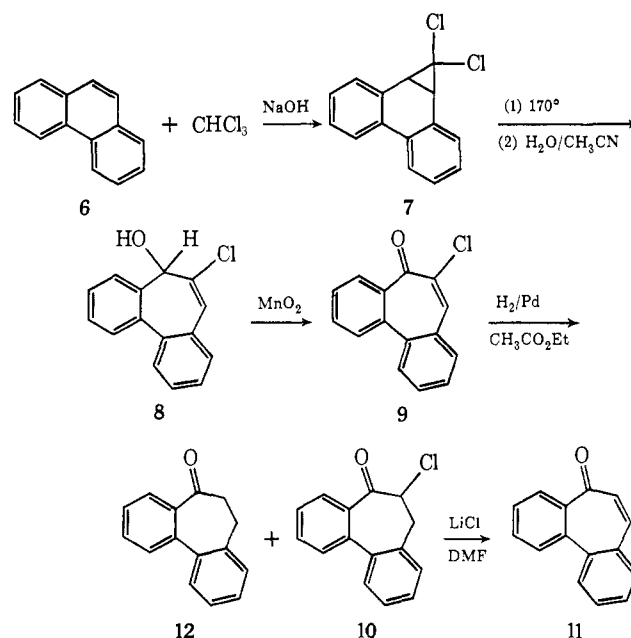

Figure 1.

proved too troublesome or expensive in our hands. Therefore, a synthetic sequence (Scheme I) based on a

Scheme I

method for preparation of 6-chloro-5H-dibenzo[a,c]-cycloheptene previously developed in our laboratories was employed. A procedure similar to that reported by Joshi, Singh, and Pande[20] allowed the accumulation of a large quantity of 7,7-dichlorodibenzo[a,c]bicyclo-[4.1.0]heptane (**7**). The alcohol **8** was obtained in quantitative yield by heating a melt at 170° for 30 min followed by basic hydrolysis. Isomerization of the alcohol **8** to the chloro ketone **10** was most conveniently accomplished by oxidation with activated manganese dioxide to the unsaturated chloro ketone **9**[21,22] (90% yield) followed by catalytic reduction (78% yield) with **12** formed as a by-product.[23]

(18) J. W. Cook, G. T. Dickson, and J. D. Loudon, *J. Chem. Soc., London*, 746 (1947).

(19) J. W. Cook, J. Jack, J. D. Loudon, G. L. Buchanan, and G. L. MacMillan, *J. Chem. Soc., London*, 1397 (1951).

(20) G. Joshi, N. Singh, and L. Pande, *Synthesis*, 317 (1972).

(21) W. E. Parham, D. A. Bolon, and E. E. Schweizer, *J. Amer. Chem. Soc.*, **83**, 603 (1961).

(22) F. Nerdel, J. Buddrus, W. Brodowski, and J. Windhoff, *Tetrahedron Lett.*, 1175 (1968).

(23) Hydrogenolysis to **12** accompanies hydrogenation and occurs especially rapidly in ethanol. In fact, catalytic reduction of the unsaturated chloro ketone **9** with 2 equiv of hydrogen in ethanol appears to be the method of choice for synthesis of 6,7-dihydro-5H-dibenzo[a,c]-cyclohepten-5-one (**12**).[18,24,25] Fortunately, when ketone **12** is formed as a side product, it can be brominated[25] and the bromo ketone used in place of chloro ketone **10** in the subsequent step.

Both ketone **12** and chloro ketone **10** have unusual nmr spectra which exhibit remarkable variation with solvent. In $CDCl_3$ the spectrum of **12** shows only aromatic protons and a sharp singlet at τ 7.00; in benzene, the upfield singlet becomes the expected AA'BB' multiplet. In benzene-d_6 the 60-MHz nmr spectrum of chloro ketone **10** shows aromatic protons, a sharp triplet at τ 4.62, and a sharp doublet at τ 7.05 ($J = 7.5$ Hz); in acetone-d_6, the spectrum is the textbook ABX pattern (τ_A 6.81, τ_B 6.48; τ_X 4.11, $J_{AB} = 13.5$ Hz, $J_{AX} = 9.0$ Hz, $J_{BX} = 4.5$ Hz); in $CDCl_3$, the ABX pattern is less obvious due to accidental coincidences.

Dehydrohalogenation to ketone **10** is readily accomplished under conditions similar to those employed by Collington and Jones[26] for the preparation of other tropones. Spectral and physical properties of the final product **11** are identical in all respects with the ketone prepared as previously reported.[18] Conversion to the tosylhydrazone and formation of the sodium salt were unexceptional.[1] The carbene **14** was generated from the salt by pyrolysis or by Pyrex-filtered photolysis.

Carbene **14** mimics the monoannelated cycloheptatrienylidene in its facile rearrangement on thermal generation in solution.[1,2] In benzene at 125° it rearranges cleanly and forms 9-(2,4,6-cycloheptatrien-1-yl)phenanthrene (**16**) quantitatively. Photolytic gen-

Scheme II
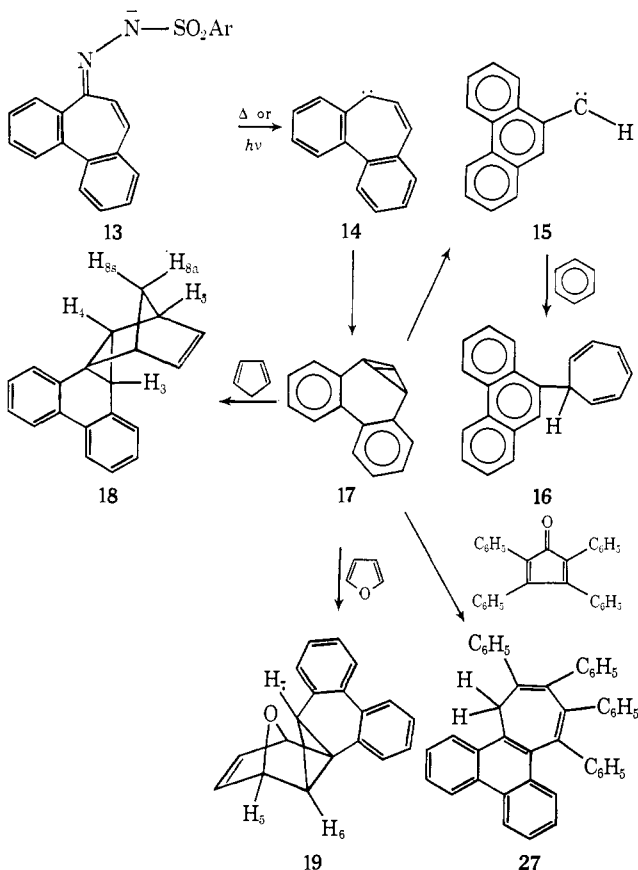
eration at room temperature in benzene also produces **16** as the major product although the yield is less than

quantitative. The rearrangement seems to be quite sluggish when the aromatic carbene is generated photolytically at −60° in 1:2 benzene/tetrahydrofuran. Under these conditions, only about 1% of the starting carbene can be accounted for as adducts of phenanthrylcarbene to either benzene or THF.[27]

Carbene **14** does not, however, react with olefins prior to rearrangement as do other aromatic carbenes such as 4,5-benzocycloheptatrienylidene (**20**)[1,2,45] and cycloheptatrienylidene (**1**).[28] Even at temperatures so low that products from the rearranged carbene **15** were isolated in only very low yield, no evidence for the expected spiro adducts to styrene or dimethyl fumarate could be obtained.

On the other hand, tetraphenylcyclopentadienone efficiently intercepts a reactive intermediate prior to formation of phenanthrylcarbene (**15**). When the tosylhydrazone salt **13** was thermolyzed in the presence of 3 equiv of tetracyclone, 10,11,12,13-tetraphenyl-9*H*-cyclohepta[e]phenanthrene (**27**) was isolated in 50% yield. This product, which is believed to arise from reaction of tetracyclone with **17**, was characterized as follows. The phenanthrene nucleus is indicated by the weak long wavelength uv absorptions and the characteristic nmr pattern of the underside protons, τ 1.25–1.6 (m, 2 H). The geminal coupling constant of the methylene protons is consistent with that generally observed in conformationally restricted cycloheptatrienes.[29] It is inconsistent with either long-range coupling or coupling between H-1 and H-7 (generally ca. 6.0–7.5 Hz). Furthermore, both the physical and spectral properties of **27** are consistent with those of 9-methoxy-6,7,8-triphenyl-5*H*-benzocycloheptene[29] which is a particularly suitable model compound. On the nmr time scale, the cycloheptatriene ring conformation is frozen at temperatures at least as high as 150°. (In the less restricted model compound, the methylene proton signals coalesce at 65°.) As with the model compound, an nmr signal due to what is apparently a trace of an H-shift isomer (methine proton at τ 4.52) results when solutions are heated to 150°. This material is also present in the crude reaction mixture and may be analogous to one of the products formed upon reaction of cycloheptatrienylidene (**1**) with tetracyclone (methine proton at τ 4.63).[30]

Other dienes were also found to capture an intermediate prior to arylcarbene formation. Thus, photolysis of the tosylhydrazone salt of **13** at −60° in the presence of cyclopentadiene or furan with tetrahydrofuran as cosolvent gave in high yield the cyclopropene Diels–Alder adducts **18** and **19** in 73 and 47% yields, respectively. If the photolysis is stopped shortly after all of the tosylhydrazone salt has decomposed, adduct **18** is the only isomer found in the cyclopentadiene reaction to a limit of detection of about 1%. Analyses and spectral properties leave little doubt about either the structure or stereochemistry of this adduct. Mass spectra and elemental analysis assure the molecular formula. An ir absorption at 1045 cm⁻¹ suggests a

(24) H. Rapoport and A. R. Williams, *J. Amer. Chem. Soc.*, **71**, 1774 (1949); C. W. Muth, W.-L. Sung, and Z. B. Papanastassiou, *ibid.*, **77**, 3393 (1955).

(25) B. Eistert and H. Minas, *Chem. Ber.*, **97**, 2479 (1964).

(26) E. Collington and G. Jones, *J. Chem. Soc. C*, 2656 (1969).

(27) Insertion into THF has been studied by J. P. Mykytka, University of Florida, unpublished results.

(28) W. M. Jones and C. L. Ennis, *J. Amer. Chem. Soc.*, **91**, 6391 (1969); E. E. Waali and W. M. Jones, *ibid.*, **95**, 8114 (1973).

(29) W. Tocktermann, G. Schnabel, and A. Mannschreck, *Z. Naturforsch.*, **218**, 897 (1966); *Justus Liebigs Ann. Chem.*, **711**, 88 (1969).

(30) H. Dürr, H. Kober, I. Halberstadt, U. Neu, T. T. Coburn, T. Mitsuhashi, and W. M. Jones, *J. Amer. Chem. Soc.*, **95**, 3818 (1973).

cyclopropane ring.[31] Saturation of the nonannelated double bond of the dibenzocycloheptatrienylidene and 1,4 addition to the diene are both indicated by the nmr spectrum in the vinyl region. The presence of a cyclopropane proton cis to the aromatic rings is supported by a 1-H doublet of doublets (H-4) at τ 9.39. The magnitude of coupling between H-4 and H-5 fixes an exo orientation for H-4 which, in turn, requires H-3 to be endo-syn. The magnitude of $J_{3,4}$ (2.8 Hz) is consistent with this orientation (for a model see tricyclo-[3.2.1.0²·⁴]octene).[32] Endo assignment to the cyclopropane is further supported by the chemical shift of the two vinyl hydrogens (ca. τ 3.95) which appear significantly upfield from vinyl hydrogens of known exo-tricyclo[3.2.1.0²·⁴]oct-6-enes but are consistent with an endo structure.[31-33] The syn cyclopropane hydrogen H-3 also has the appropriate chemical shift (τ 7.49).[33] Finally, were H-3 anti in adduct 18, long-range coupling to H-8 (anti) would be expected.[31,35] The very sharp doublet observed ($J_{3,4}$ = 2.8 Hz) even in an expanded 100-MHz spectrum and the lack of any change in this portion of the spectrum when either methylene bridge proton is irradiated belies the possibility that H-3 is endo-anti. Unassailable proof that the isomer formed has the endo configuration with H-3 syn is essential to the contention that this compound results from a Diels–Alder reaction of the cyclopropene intermediate 17 with cyclopentadiene since there is no precedent for the formation of any other stereoisomer in cycloaddition reactions of 3-monosubstituted cyclopropenes with cyclopentadiene.[30,34,36,37]

In formation of the furan adduct 19, the reaction was not as clean as with cyclopentadiene. Although the exo adduct 19 was the major product, there were also formed a number of unidentified minor products and as a result it is not possible to exclude formation of a small amount of endo isomer which would presumably be the less stable isomer[38] in this case. The spectral characteristics of this major adduct (see Experimental Section) establish its gross structure and the following subtleties permit a stereochemical conclusion. No coupling is observed in the nmr spectrum between the cyclopropyl hydrogen (H-6) and the adjacent bridgehead proton (H-5) as would be expected if H-6 were endo,[39,42] and the abnormally low-field position of H-7 (τ 6.39) requires its proximity to the bridging oxygen[40,41] (cf. the analogous proton of adduct 18 at τ 7.49).

The assigned stereochemistry is further supported by a study of lanthanide-induced proton nmr shifts. Ad-

dition of a small amount of Eu(fod)₃ to an nmr solution containing adduct 19 produced a downfield shift of H-7 of even greater magnitude than that experienced by the alkoxy protons at the bridgehead positions. A rough calculation[43] of the agreement factor[44] for the endo isomer (R = 0.36) and for the exo isomer 19 (R = 0.05) provides convincing evidence that the molecular geometry is that shown.

Although the best yields of adducts 18 and 19 are obtained at low temperatures, and volatile and reactive dienes are most conveniently employed below room temperature, the formation of these adducts is possible at any temperature at which carbene 14 undergoes rearrangement. For example, photolysis of the tosylhydrazone salt 13 at room temperature in neat furan produced 43% of the adduct 19, while pyrolysis at 115° in a sealed tube gave 11% of the adduct. In each case only the exo isomer was detected. Unfortunately, adduct 19 is thermally unstable at the temperature necessary for thermal formation of the carbene. Tetracyclone is a much better trap for the thermally generated intermediate. On the other hand, no trace of adduct 19 was detected when the arylcarbene 15 was generated directly from its tosylhydrazone salt in the presence of furan under any of these conditions.

In an attempt to at least qualitatively assess the lifetime of the diannelated bicyclo[4.1.0]heptatriene 17, two low-temperature (−60°) photolyses were carried out in the absence of diene for 7 min each, the light was extinguished and cold (−78°) cyclopentadiene was added immediately in one run and after 2 min in the other. The yields of 18 were 4.7 and 3.6%, respectively. In a third experiment, the photolysis was allowed to proceed for 20 min before extinguishing the light. In this case, addition of furan gave no detectable 17.

At low temperatures in the presence of olefins 4,5-benzocycloheptatrienylidene (20) can be trapped to give spiro compounds. Although the yield is poor, cyclohexene,[1,2] dimethyl fumarate,[45] styrene,[45] and substituted styrenes[45] have been successfully used. As the temperature is raised, the yield of products resulting from the rearranged carbene 26 increases. When 4,5-benzocycloheptatrienylidene (20) was generated photolytically at −60° in the presence of cyclopentadiene, a small amount (16%) of endo-5,6-benzotetracyclo[7.2.-1.0²·⁷.0²·⁸]dodeca-3,5,10-triene (22) was obtained. This is the product expected from reaction of the cyclopropene intermediate 21 with cyclopentadiene in a Diels–Alder reaction. The geometry of the adduct follows from a comparison of its nmr spectrum with 18. A structure proof similar to that presented for adduct 18 is equally satisfactory in every detail (see Experimental Section).

Thermal generation of carbene 20 in the presence of tetraphenylcyclopentadienone gave a low yield (9%) of 7,8,9,10-tetraphenyl-9H-cyclohepta[a]naphthalene (28) along with major products that are 1:1 adducts that have retained CO (mol wt) 524 by mass spectrum; cor-

(31) S. C. Clarke, K. J. Frayne, and B. L. Johnson, Tetrahedron, 25, 1265 (1969).
(32) R. R. Sauers and P. E. Sonnet, Chem. Ind. (London), 786 (1963); Tetrahedron, 20, 1029 (1964).
(33) The best model for this compound is endo-2,3,4-triphenyltricyclo[3.2.1.0²·⁴]oct-6-ene with the 3-phenyl anti.³⁴ In its spectrum the vinyl protons appear at τ 3.77 and the syn cyclopropane hydrogen at τ 7.44.
(34) M. A. Battiste, Tetrahedron Lett., 3795 (1964).
(35) K. Tori and M. Ohtsuru, Chem. Commun., 886 (1966).
(36) R. M. Magid and S. E. Wilson, J. Org. Chem., 36, 1775 (1971).
(37) G. L. Closs, Advan. Alicyclic Chem., 1, 53 (1966).
(38) There are a number of previous reports of cyclopropanes reacting with furans to yield only the exo (endo-epoxy) adduct.³⁹⁻⁴¹
(39) M. F.-N. Neumann and C. Buchecker, Angew. Chem., Int. Ed. Engl., 9, 526 (1970).
(40) D. L. Longone and D. M. Stehouwer, Tetrahedron Lett., 1017 (1970).
(41) R. Breslow, G. Ryan, and J. T. Groves, J. Amer. Chem. Soc., 92, 988 (1970).
(42) R. LaRochelle and B. M. Trost, Chem. Commun., 1353 (1970).
(43) The lanthanide atom was assumed to be directly above the oxygen at 3.0 Å distance in the plane bisecting the bridge; distances and angles were measured manually from a Dreiding model. Only nonaromatic protons and shift data at maximum mole ratio Eu(fod)₃/19 were used in the computation.
(44) M. R. Willcott, III, R. E. Lenkinski, and R. E. Davis, J. Amer. Chem. Soc., 94, 1744 (1972).
(45) Unpublished work of L. W. Christensen.

Scheme III

Scheme IV

IV (for carbene **20**).[48]   Although this requires one step
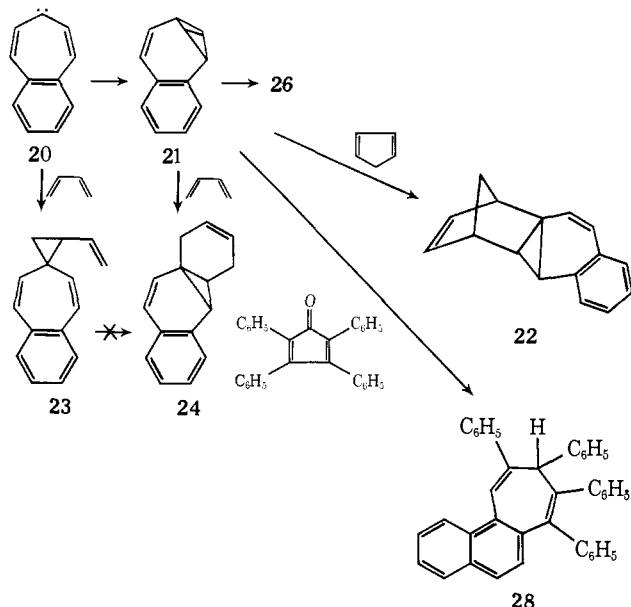
rect elemental analysis). These products, none of which were found to be precursors to **28**, most likely result from the rearranged carbene **26** (for example, β-naphthyltetraphenylphenol is one product). In addition to correct elemental analysis, **28** also showed spectral properties consistent with the assigned structure. In particular, the methine proton appears at τ 4.57 which is in line with similar structures obtained from reaction of both carbene **1**[30] and **14** with tetracyclone (τ 4.63 and 4.52, respectively).

Reaction of 4,5-benzocycloheptatrienylidene (**20**) with 1,3-butadiene at −60° gave two isomeric hydrocarbons **23** and **24**. The major product was shown to be 4,5-benzotricyclo[5.4.0.0^{1,6}]undeca-2,4,9-tetraene (**24**) by elemental analysis, high resolution mass spectrometry nmr analysis (see Experimental Section), and comparison of its spectra with those of appropriate models including a benzonorcaradiene incorporated into a 3-norcarene[46,47] and the cyclopropene adducts previously discussed. However, a minor isomer was also isolated and was assigned structure **23** (1-vinyl-6,7-benzospiro[2.6]nona-4,6,8-triene) based on high resolution mass spectrometry and comparison of its spectra (see Experimental Section) with those of a number of models.[1,2,45] Particularly notable are the similarities between this adduct and adducts of benzocycloheptatrienylidene (**20**) and cycloheptatrienylidene (**1**) with styrene and other simple olefins.[28,29,45] Compound **23** is stable enough to permit molecular distillation at 70°; furthermore, subjecting it to the conditions of the addition reaction gave no detectable trace (<1%) of **24**. **23** was recovered (75%) unchanged.
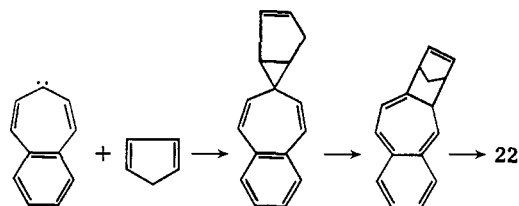
Discussion

In principle, the observed diene adducts (**18, 19, 22, 27, 28,** and **24**) could be formed by either initial closure of the mono- and dibenzocycloheptatrienylidenes (**14** and **20**) to the corresponding bicycloheptatrienes (**17** and **21**) or simple addition of the carbene to one double bond followed by the rearrangement depicted in Scheme

in which benzene aromaticity is destroyed, it is a mechanism that merits serious consideration, especially in light of the reported[28] rearrangement of the adduct of cycloheptatrienylidene and cis-pentadiene. The failure to detect any spiro adducts when **14** was generated in the presence of olefins argues against such a mechanism

Scheme V
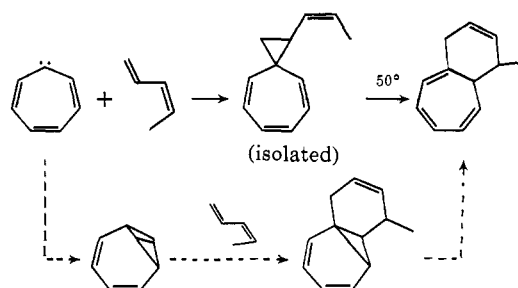
in the case of the dibenzocycloheptatrienylidene. Also, isolation of **23** and demonstration of its stability to reaction conditions vitiate this possibility for formation of **24** and increase the credibility of the bicycloheptatriene mechanism for all of the annelated systems.

Additional support for a bicycloheptatriene cycloaddition mechanism for formation of **18, 19,** and **22** is found in their stereochemistry. Thus, endo-anti stereochemistry appears to be characteristic of the addition of 3-substituted cyclopropenes to cyclopentadiene[34,36,37] while the opposite is often favored for additions to furan.[39-41] A third possible mechanism for formation of the diene adducts of the annelated carbenes is 2 + 4 addition of an allene or zwitterion followed by isomerization of the resultant unstable polyene to the ob-

served dibenzonorcaradienes. Although there is no definitive evidence against this possibility, it is worth noting that the observed increase in 2 + 4 adduct upon additional annelation is opposite to what would be expected of a mechanism that requires destruction of benzene aromaticity.[14b] The evidence[28] that cycloheptatrienylidene (**1**) (which does not undergo carbene–carbene rearrangement in solution) does not add to dienes as an allene or zwitterion further weakens a hypothesis that annelated carbenes react as such.

The evidence presented strongly favors formation of the fused cyclopropene intermediates from intramolecular reaction of carbenes **14** and **20**. Furthermore,

(46) R. Huisgen and G. Juppe, *Chem. Ber.*, **94**, 2332 (1961).
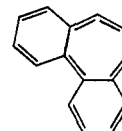(47) J. A. Berson and E. S. Hand, *J. Amer. Chem. Soc.*, **86**, 1978 (1964).
(48) It should be noted that whatever the mechanism, product formation cannot result from a secondary photoreaction since the same products were formed when the carbenes were generated either thermally or photochemically.

from the yields of adducts, it is clear that irreversible cyclopropene formation and irreversible rearrangement cannot be competitive modes of destruction available to these aromatic carbenes. Thus, when formed by thermolysis at 120 ± 10°, dibenzo[a,c]cycloheptatrienylidene (14) rearranges and is trapped in 95% yield as the benzene addition product 16 of phenanthrylcarbene. This permits no more than 5% irreversible formation of cyclopropene 17. However, under similar (120 ± 10°) thermolysis conditions, the Diels–Alder adduct 27 of cyclopropene 17 and tetracyclone is isolated in 50% yield, thus vitiating any possibility of competitive irreversible cyclopropene formation which does not lead to the arylcarbene. On the other hand, it is considerably more difficult to show that carbenes 14 and 20 are not in rapid equilibrium with their respective cyclopropenes with rearrangement occurring by a different mechanism. The photochemical Wolff rearrangement[49] is a pertinent example. Although an oxirene intermediate (or transition state) is certainly formed, it does not produce the rearranged product. Oxirenes in carbonylcarbene rearrangements may, in fact, offer a very close analogy to cyclopropenes in aromatic carbene rearrangements. Both may be side species not involved in the rearrangement.

However, some reasons for rejecting this possibility for carbene–carbene rearrangements can be offered. In the first place, cyclopropene trapping appears to go hand in hand with rearrangement in that evidence for trapping (which has only been observed in solution) has only been obtained in the case of those carbenes that rearrange in solution. Evidence for cyclopropene trapping from cycloheptatrienylidene (which does not rearrange in solution) is lacking.

Second, the minimum conditions necessary for carbene–carbene rearrangement can be identified with cyclopropene stability.

For example, the facile rearrangement of the methanoannulenylcarbene[5] (34) may be ascribed to the rela-

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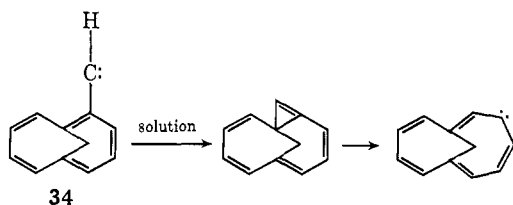
tively unstrained cyclopropene required. Furthermore, the influence of benzannelation on carbene–carbene rearrangements can be rationalized in terms of the moderating effect of benzene rings on the loss of resonance energy during the process of forming the cyclopropenes. Thus, using cations as (highly oversimplified) models for carbenes and linear polyenes (with appropriate annelation) for the trienes, simple Hückel calculations[50,51] predict cycloheptatrienylidene (1) would lose 2.00 β of resonance energy upon closure whereas 20 and 14 would lose 1.77 and 1.65 β, respectively. Since these losses would probably be reflected in the transition states, it is reasonable to expect cyclo-

heptatrienylidene closure to be slower than its annelated relatives. Of course, closure is not necessarily endothermic in spite of the loss in resonance energy since a new (although strained) σ bond is formed.

Interestingly enough, the same order also pertains for loss of resonance energy upon closure of the three arylcarbenes (phenylcarbene, naphthylcarbene, and phenanthrylcarbene) to bicycloheptatrienes. However, none of these carbenes show any evidence of closure to the bicycloheptatrienes in solution when generated either thermally or photolytically. This is probably due to the facility of reaction of the arylcarbenes with solvent or other substrates. The effect of annelation on the position of equilibrium between aromatic and arylcarbenes has been discussed elsewhere.[14b]

At this time relatively little is known about the properties of the highly strained bicyclo[4.1.0]heptatriene ring system. Certainly, from this work it is apparent that even at very low temperatures the cyclopropene moiety of the mono- and dibenzobicycloheptatrienes undergoes quite facile addition to dienes to give typical Diels–Alder adducts. Furthermore, although apparently rather short lived even at −60°, the diannelated system (which should be the longest lived) has a half-life of at least a few minutes as evidenced by trapping by cyclopentadiene (in low yield) even after the photolysis lamp was extinguished. The low yield in these experiments may well reflect only the photolability of arylsubstituted cyclopropenes[52] rather than an inherent thermal instability of the intermediate.

At room temperature and above and in the absence of dienes, ring opening to carbenes[53] apparently becomes the dominant reaction of both mono- and dibenzobicycloheptatrienes. From the work reported herein, the annelated systems apparently preferentially open to the arylcarbenes.

Diene trapping experiments such as those employed here offer a means of testing the mechanistic similarity of other rearrangements which have been postulated to involve carbene–carbene interconversions. For example, it might be fruitfully applied to the base promoted reorganization of ferrocenyltropylium fluoroborate[54] or, perhaps, even the often postulated[55,56] 2H-azirine intermediate in the rearrangement of arylnitrenes to azepines.

Experimental Section

General. Melting points were taken in a Thomas-Hoover Unimelt apparatus and are uncorrected. Elemental analyses were performed by Atlantic Microlab, Inc., Atlanta, Ga. Accurate mass measurements were provided by the High Resolution Mass Spectrometry Laboratory, Florida State University, Tallahassee,

(49) J. Fenwick, G. Frater, K. Ogi, and O. P. Strausz, J. Amer. Chem. Soc., 95, 124 (1973); and references cited.

(50) A. Streitwieser, Jr., and J. I. Brauman, "Supplemental Tables of Molecular Orbital Calculations," Vol. I, Pergamon Press, London, 1965.

(51) C. A. Coulson and A. Streitwieser, Jr., "Dictionary of π-Electron Calculations," Vol. II, Pergamon Press, London, 1965.

(52) L. Schrader and W. Hartmann, Tetrahedron Lett., 3995 (1973).

(53) Ring opening to give either aromatic or arylcarbenes is simply an example of the well known thermal opening of cyclopropenes to vinylcarbenes.[37] The fact that these openings apparently occur so much faster than most cyclopropenes is probably primarily due to the resonance energy gained by aromatization. From models, the bicycloheptatriene ring system may also experience some additional torsional strain (above the normal cyclopropene and cyclohexadiene strains) but this does not appear to be very significant.

(54) A. Ashkenazi, S. Lupan, A. Schwarz, and M. Cais, Tetrahedron Lett., 817 (1969).

(55) M. Appl and R. Huisgen, Chem. Ber., 92, 2961 (1959); W. von E. Doering and R. A. Odum, Tetrahedron, 22, 81 (1966).

(56) An initial attempt in collaboration with M. Battiste and R. Moerck has provided a tentative indication for the presence of a 2H-azirine in the pyrolysis of phenylnitrene and will be reported subsequently.

Fla. Ultraviolet and visible spectra were recorded on a Cary 15 double-beam spectrophotometer using 1-cm silica cells. Infrared spectra were recorded with a Beckman IR-10 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. A Varian XL-100 spectrometer was used for double resonance experiments and for some studies with lanthanide shift reagents. Chemical shifts are reported in τ values from internal tetramethylsilane standard. Low-resolution mass spectra were determined on a Hitachi Model RMU-6E mass spectrometer.

Analytical thin-layer chromatography (tlc) was accomplished on 2 in. × 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 in. × 8 in. plates coated with 1.0-mm layers of HP-254 silica gel. Components were visualized by their quenching of fluorescence under uv light. Analytical gas–liquid chromatography was accomplished with a Varian Aerograph Series 1200 flame ionization instrument using a 10 ft × $^1/_8$ in. or a 5 ft × $^1/_8$ in. column of 5% SE-30 on Chromosorb W AW DMSC. Analytical results were obtained by cutting and weighing Xerox copies of the chromatograms. Preparative gas–liquid chromatography was carried out on a Varian Aerograph 90-P thermal conductivity instrument using a 18 ft × $^1/_4$ in. column of 20% SE-30 on Chromosorb W. MCB grade G2 silica gel or activity grade 111 Woelm basic alumina was used for column chromatography.

All chemicals are reagent grade used as supplied unless otherwise stated. Dioxane and tetrahydrofuran were dried by distillation from lithium aluminum hydride and passage over activity grade I Woelm basic alumina with subsequent storage over calcium hydride under a nitrogen atmosphere. 1,3-Cyclopentadiene was prepared in the standard way[57] from dicyclopentadiene previously dried over magnesium sulfate or 4A molecular sieve. It was stored at Dry Ice temperature over sodium sulfate under nitrogen and used within two weeks. Practical grade furan was washed with 5% sodium hydroxide, dried over calcium sulfate, distilled from KOH, passed through basic alumina (Woelm, grade 1), and stored under nitrogen. Diethylamine and butylamine were distilled from lithium aluminum hydride or sodium hydroxide and passed through a short grade 1 Woelm basic alumina column.

7,7-Dichlorodibenzo[a,c]bicyclo[4.1.0]heptane (7). A modified procedure of Joshi, Singh, and Pande was employed.[20] Centrimide (Pfaltz and Bauer, Inc.) was used as the cationic detergent (0.7 g of Centrimide to 100 g of phenanthrene) and the reaction was run to completion by stirring 15 hr at room temperature. Prior to recrystallization the product was decolorized by eluting rapidly through a large silica gel column with carbon tetrachloride. 7 obtained (89.9 g, 58% yield) was identical in all respects with that previously characterized: mp 144–145° (lit. 140.2[58] and 141.2° [20]) (melting occurs with decomposition and is a function of the rate of heating).

6-Chloro-5H-dibenzo[a,c]cyclohepten-5-ol (8). 7,7-Dichlorodibenzo[a,c]bicyclo[4.1.0]heptane (7) (5.85 g, 22.4 mmol) was thermolyzed under nitrogen at 170 ± 5° in an oil bath for 30 min. The resultant oil was taken up in 100 ml of acetonitrile, and 130 ml of saturated sodium bicarbonate solution was added. The two-phase reaction mixture was stirred rapidly at room temperature for 1 hr as a salt precipitated. After dilution with 100 ml of water, the solution was extracted with three 75-ml portions of methylene chloride. The combined organic extracts were dried over anhydrous sodium sulfate and filtered. Solvent was removed to yield 5.46 g (22.4 mmol, quantitative) of alcohol 8 suitable for further use. Sublimation (150° (0.15 mm)) followed by grinding under pentane gave colorless crystals of analytical purity: mp 80.5–81.5°; uv, λ_{max} (C₂H₅OH) 239 nm (ϵ 41,000); ir (melt) 3420, 3060, 1625, 1480, 1085, 755, 730 cm⁻¹; ¹H nmr (CDCl₃) τ 2.3–2.9 (m, 8 H), 3.31 (s, 1 H), 4.12 (d, J = 6 Hz, 1 H), 7.26 (d, J = 6 Hz, 1 H); mass spectrum, m/e 242 (M⁺).

Anal. Calcd for C₁₅H₁₁ClO: C, 74.23; H, 4.68; Cl, 14.60. Found: C, 74.35; H, 4.71; Cl, 14.75.

6-Chloro-5H-dibenzo[a,c]cyclohepten-5-one (9). Activated manganese dioxide (Winthrop Laboratories, 30.0 g, 330 mmol) and 6-chloro-5H-dibenzo[a,c]cyclohepten-5-ol (8) (5.27 g, 21.8 mmol) were stirred in 200 ml of methylene chloride at room temperature under nitrogen for 1 hr. Anhydrous calcium sulfate was added,

and the mixture was suction filtered through Celite 545. The residue was washed throughly with 500 ml of ethyl acetate. Solvent was removed and the oil column chromatographed on silica gel with carbon tetrachloride–methylene chloride (4:1). The crystalline product (9) obtained after solvent removal (4.69 g, 19.5 mmol, 90% yield) was suitable for further use.

Recrystallization from benzene–heptane gave analytically pure 9: mp 98.0–98.8° (lit.[21,22] 95.5–97.0 and 98°); ir (KBr) 1665, 1605, 1595 cm⁻¹ (lit.[21,22] 1665, 1610, 1595 cm⁻¹); ¹H nmr (CDCl₃) τ 2.0–2.7 (m); mass spectrum, m/e 240 (M⁺). On contact, 9 is an annoying skin irritant.

6-Chloro-6,7-dihydro-5H-dibenzo[a,c]cyclohepten-5-one (10). Catalytic hydrogenation of 6-chloro-5H-dibenzo[a,c]cyclohepten-5-one (9) (4.59 g, 19.1 mmol) was carried out over 5% palladium on carbon (0.75 g) in 75 ml of ethyl acetate containing 1 ml of glacial acetic acid using a standard atmospheric pressure hydrogenation apparatus.[59] Hydrogen (468 ml, uncorrected for solvent vapor) was taken up in 3.4 hr at 1 atm of pressure and at 24°. The reaction mixture was filtered through sodium carbonate (anhydrous) and washed with ethyl acetate, and the solvent was removed. The crude product mixture consisted of 20% unreacted starting material 9, 67% desired product 10, and 13% of a product formed on further hydrogenolysis, 6,7-dihydro-5H-dibenzo[a,c]cyclohepten-5-one (12). The desired product 10 contaminated with 16% starting material (3.57 g) eluted as the first major component from a silica gel column with carbon tetrachloride. Recrystallization from ethanol–water yielded 10 (3.08 g, 12.7 mmol, 76% yield), and a portion of starting material was recovered (0.52 g).

Analytically pure 10 was obtained after a second recrystallization from ethanol–water: mp 89–90°; uv, λ_{max} (C₂H₅OH) 305 nm (ϵ 1,600), 238 (24,000); ir (KBr) 3060, 3020, 2920, 1695, 1595, 1205, 920, 800, 795, 655 cm⁻¹; ¹H nmr (benzene-d₆) τ 2.3–2.6 (m, 2 H), 2.7–3.2 (m, 6 H), 4.62 (t, J = 7.5 Hz, 1 H), 7.05 (d, J = 7.5 Hz, 2 H); ¹H nmr (acetone-d₆) τ 2.1–2.7 (m, 8 H), 4.11 and 7.03–6.29 (ABX pattern, ν_A = τ 6.81, ν_B = τ 6.48, ν_X = τ 4.11, J_{AB} = 13.5 Hz, J_{AX} = 9.0 Hz, J_{BX} = 4.5 Hz, 3 H); ¹H nmr (CCl₄) τ 2.3–2.9 (m, 8 H), 4.52, and 6.6–7.1 (unusual ABX pattern, ν_A = τ 6.84, ν_B = τ 6.61, ν_X = τ 4.52, J_{AB} = 13.5 Hz, J_{AX} = 12 Hz, J_{BX} = 3 Hz, 3 H); mass spectrum, m/e 242 (M⁺), 180 (M⁺ − COCl, major peak).

Anal. Calcd for C₁₅H₁₁ClO: C, 74.23; H, 4.68; Cl, 14.60. Found: C, 74.02; H, 4.73; Cl, 14.53.

6,7-Dihydro-5H-dibenzo[a,c]cyclohepten-5-one (12). (a) This material was eluted as the second major component off the silica gel column with carbon tetrachloride containing increasing amounts of methylene chloride as eluent. 12 (0.33 g, 1.6 mmol, 10% yield) was obtained after recrystallization from methanol–water. Sublimation gave analytically pure material: mp 85.0–85.8° (lit.[24] 85–86°).

(b) 6-Chloro-5H-dibenzo[a,c]cyclohepten-5-one (9) (0.175 g, 0.729 mmol) was catalytically reduced on 5% palladium on charcoal (0.034 g) in 12 ml of absolute ethanol containing anhydrous sodium acetate (0.150 g, 1.83 mmol). Two equivalents of hydrogen (35.7 ml at 1 atm and 24°) were taken up in 40 min at which point hydrogenation ceased. The reaction mixture was filtered, and the solvent was removed. Sublimation (80° (0.15 mm)) gave analytically pure 12 (0.144 g, 0.547 mmol, 82% yield) identical with that obtained by procedure a: mp 85–86° (lit.[24] 85–86°); ir (melt) 3060, 2930, 1675, 1595, 1445, 1265, 750 cm⁻¹ (lit.[24] $\nu_{C=O}$ 1678 cm⁻¹); ¹H nmr (CDCl₃) τ 2.2–2.8 (m, 8 H), 7.00 (s, 4 H); ¹H nmr (benzene-d₆) τ 2.05–2.3 (m, 1 H), 2.7–3.2 (m, 7 H), 7.2–7.7 (m with AA'BB' pattern, 4 H); mass spectrum, m/e 208 (M⁺), 207 (major peak), 180 (M⁺ − CO).

5H-Dibenzo[a,c]cyclohepten-5-one (11). To a solution of anhydrous lithium chloride (13.0 g, 400 mmol) in 200 ml of dimethylformamide (dried over 4A sieve) was added 6-chloro-6,7-dihydro-5H-dibenzo[a,c]cyclohepten-5-one (10) (3.03 g, 12.5 mmol), and the solution was stirred at reflux under nitrogen for 15 hr. The solvent was distilled off until lithium chloride began to precipitate. The pot residue was diluted with 300 ml of water and extracted with three 40-ml portions of methylene chloride. The organic extracts were combined and dried over anhydrous magnesium sulfate. Filtration and solvent removal left a viscous oil from which the last bit of dimethylformamide was removed *in vacuo*. The oil was column chromatographed on silica gel with carbon tetrachloride containing increasing amounts of chloroform. Crystalline 11 was obtained

(57) R. C. Moffett, "Organic Synthesis," Collect. Vol. IV, Wiley, New York, N. Y., 1963, p 238.

(58) G. C. Joshi, N. Singh, and L. M. Pande, *Tetrahedron Lett.*, 1461 (1972).

(59) K. B. Wiberg, "Laboratory Techniques in Organic Chemistry," McGraw-Hill, New York, N. Y., 1960, pp 228–231.

after solvent removal (2.20 g, 10.7 mmol, 85% yield). Sublimation (120° (0.2 mm)) gave white crystals (1.93 g) with the following properties: mp 83–84.5° (lit.[19] 83–85°); ir (KBr) 3060, 3030, 1640, 1590, 1405, 1295, 790, 785, 770, 755, 740, 730, 570 cm⁻¹ (identical with a published spectrum[60]); ¹H nmr (CDCl₃) τ 1.9–2.8 (m, 9 H), 3.35 (d, J = 12 Hz, 1 H); mass spectrum, m/e 206 (M⁺), 178 (M⁺ − CO, major peak).

Preparation of Tosylhydrazones. Benzaldehyde free tropone was prepared by the hydrolysis procedure of Harmon and Coburn[61] and converted to the tosylhydrazone as previously described.[28] 4,5-Benzotropone tosylhydrazone was synthesized in the reported manner.[1] New tosylhydrazones were prepared in the conventional way by stirring equal molar quantities of tosylhydrazide and the aldehyde of ketone in absolute ethanol (1 g/30 ml) with a drop of concentrated sulfuric acid for 15 to 20 hr.[1] The following products were obtained after recrystallization from ethanol. 5H-Dibenzo[a,c]cyclohepten-5-one tosylhydrazone: 94% yield; mp 192–195° dec; ir (KBr) 3205, 3060, 1631, 1595, 1170, 1082, 760, 740, 670, 610 cm⁻¹; ¹H nmr (DMSO-d₆) τ 0.39 (bs, 1 H), 2.1–2.8 (m, 12 H), 2.85–3.4 (d of doublets, 2 H), 7.67 (s, 3 H); mass spectrum, m/e 374 (M⁺), 190 (major peak). Anal. Calcd for C₂₂H₁₈N₂O₂S: C, 70.57; H, 4.85; N, 7.48. Found: C, 70.42; H, 4.96; N, 7.25. Phenanthrene-9-carboxaldehyde tosylhydrazone: 95% yield; mp 161–167° dec; ir (KBr) 3190, 3070, 1640, 1600, 1500, 1455, 1170, 935, 744, 580 cm⁻¹; ¹H nmr (DMSO-d₆) τ 1.7 (bs, 1 H), 1.0–1.5 (m, 4 H), 1.8–2.7 (m, 10 H), 7.67 (s, 3 H); mass spectrum, m/e 374 (M⁺), 190 (major peak). Anal. Calcd for C₂₂H₁₈N₂O₂S: C, 70.57; H, 4.85; N, 7.48. Found: C, 70.66; H, 4.90; N, 7.40.

Preparation of Sodium Salts of Tosylhydrazones. The sodium salts were prepared in the drybox under a nitrogen atmosphere by dissolving the tosylhydrazone in dry tetrahydrofuran (ca. 2 g/50 ml) and adding 1.1 equiv of sodium hydride (57% in mineral oil; Alfa Inorganics) slowly with stirring. Stirring was continued for an additional 1 hr. An equal volume of spectrograde pentane was added, and the resulting precipitate was filtered, dried under vacuum, and stored in a dark bottle in the drybox. The preparation was assumed to be quantitative and further reactions are based on weight of tosylhydrazone consumed.

Thermolysis and Photolysis of Aldehyde and Ketone Tosylhydrazone Sodium Salts. Thermolyses were carried out in a sealed tube (a 3- or 1-oz Fisher-Porter Aerosol Compatibility Tube) containing a magnetic stirring bar. The tube was well flushed with nitrogen and charged in the drybox. The thermolysis temperature was maintained within ±5° in a preheated silicone oil bath. After cooling to room temperature the tube was vented to a gas buret that permitted a determination of nitrogen evolution. For small scale photolyses (0.1–0.4 g), an apparatus having two Pyrex tubes sealed into a small volume cooling jacket 3 cm apart was employed. A 550-W Hanovia "High-Pressure Quartz Mercury-Vapor Lamp" was placed in one tube, and the other tube of 35-ml maximum volume was used as the reaction vessel. An electric stirrer was inserted through one of two ground glass inlets to the reaction vessel. A nitrogen atmosphere was maintained via the other inlet. For room-temperature photolyses, the apparatus was immersed in a water bath and a tap water flow through the cooling jacket controlled the temperature at 30 ± 5°. For low-temperature photolyses, the apparatus was immersed in a Dry Ice–methanol bath and methanol cooled with Dry Ice was circulated through the cooling jacket by a magnetic drive centrifugal pump. The temperature was thus held at −60 ± 5°. Solutions were thermolyzed or photolyzed for lengths of time in substantial excess of that necessary for complete decomposition of the salt.

9-(2,4,6-Cycloheptatrien-1-yl)phenanthrene (16). (a) 5H-Dibenzo[a,c]cyclohepten-5-one tosylhydrazone sodium salt (0.16 g, 0.40 mmol) was heated with stirring in 35 ml of reagent grade benzene for 2 hr at 125° in a sealed tube. A quantitative evolution of nitrogen (9.7 ml at 24° (1.00 atm), 0.40 mmol) resulted, and on filtration a quantitative yield of sodium toluenesulfinate dihydrate (0.088 g, 41 mmol) was collected with ir spectrum (KBr) identical with that reported.[53] The oil obtained after solvent evaporation (0.102 g, 0.38 mmol, 95% yield) was primarily the single material, 9-(2,4,6-cycloheptatrien-1-yl)phenanthrene (16), by nmr and tlc (trace amounts of H-shift isomers and cycloheptatriene to toluene re-

(60) G. Naville, H. Strauss, and E. Heilbronner, Helv. Chim. Acta, 43, 1221 (1960).

(61) K. M. Harmon and T. T. Coburn, unpublished results, 1969; see T. Ikemi, T. Hozoe, and H. Sugiyama, Chem. Ind. (London), 932 (1960).

arrangement products are apparently the only impurities). Two successive preparative layer chromatography separations (pentane, three elutions) yielded 16 as the most rapidly moving, major component. Recrystallization of the solid obtained from hexane and then from methanol gave analytically pure 16 (0.025 g, 0.093 mmol, 23% yield): mp 127–128°; uv, λmax (isooctane) 348 nm (ε 390), 341 (sh, 340), 339 (370), 332 (540), 324 (sh, 520), 297 (12,400), 285 (11,600), 276 (16,600), 254 (61,300), 247 (53,600), 222 (31,400); ir (KBr) 3060, 3030, 3010, 2850, 1600, 1490, 1450, 1430, 1255, 1145, 950, 900, 885, 770, 745, 730, 710, 700, 620, 415 cm⁻¹; ¹H nmr (CDCl₃) τ 1.2–1.5 (m, 2 H), 1.8–2.7 (m, 6 H), 3.15–3.3 (narrow d of doublets, 2 H), 3.5–3.85 (m, 2 H), 4.2–4.5 (d of doublets, 2 H), 6.4–6.7 (broad t, 1 H); mass spectrum, m/e 268 (M⁺, 100), 267 (M⁺ − 1, 68).

Anal. Calcd for C₂₁H₁₇: C, 93.99; H, 6.0. Found: C, 93.73; H, 6.11.

(b) Room-temperature photolysis of 5H-dibenzo[a,c]cyclohepten-5-one tosylhydrazone sodium salt (0.10 g, 0.25 mmol) for 50 min in 30 ml of benzene produced after filtration and solvent evaporation a yellow oil from which, after preparative layer chromatography (pentane, three elutions), 9-(2,4,6-cycloheptatrien-1-yl)phenanthrene (16) (0.035 g, 0.13 mmol, 52% yield) was isolated. Recrystallization (hexane) gave pure product with physical and spectral properties identical with those of 16 formed by thermolysis of the salt (see (a) above).

(c) Low-temperature photolysis at −60° of 5H-dibenzo[a,c]cyclohepten-5-one tosylhydrazone sodium salt (0.10 g, 0.25 mmol) in 27 ml of a 1:2 solution of benzene–tetrahydrofuran was carried out for 50 min, warmed to room temperature, and worked up in a similar manner. 9-(2,4,6-Cycloheptatrien-1-yl)phenanthrene (16) (3–10 × 10⁻⁵ g, 1.3 × 10⁻⁴ mmol, 0.04–0.13% yield) was isolated by preparative layer chromatography (pentane, three elutions) and quantitatively determined by uv spectroscopy.

Low-Temperature Photolysis of 5H-Dibenzo[a,c]cyclohepten-5-one Tosylhydrazone Sodium Salt in Tetrahydrofuran. 5H-Dibenzo[a,c]cyclohepten-5-one tosylhydrazone sodium salt (0.10 g, 0.25 mmol) was photolyzed 1 hr at −60° in 15 ml of dry tetrahydrofuran. The yellow reaction mixture was warmed to room temperature and filtered. Solvent was evaporated. An nmr spectrum of the residue indicated a low yield of chloroform soluble products, predominantly if not completely aromatic proton resonances were observed (<10% phenanthryl); tlc (cyclohexane–benzene, 2:1) showed numerous components with a good deal of streaking. Isolation and characterization of these compounds has not been completed.

Low-Temperature Photolysis of the Sodium Salt of 5H-Dibenzo[a,c]cyclohepten-5-one Tosylhydrazone in the Presence of Styrene. 5H-Dibenzo[a,c]cyclohepten-5-one tosylhydrazone sodium salt (0.16 g, 0.40 mmol) was photolyzed for 1 hr at −60° in 15 ml of dry tetrahydrofuran containing styrene (2.50 g, 24.0 mmol, inhibitor removed by passing through grade 1 Woelm alumina). The solution was warmed to room temperature and suction filtered. The solvent was evaporated and styrene removed in vacuo at room temperature. Nmr and tlc of the residue were very similar to those of the product mixture obtained from photolysis in the absence of styrene (no vinyl protons in the nmr to a limit of detection of ∼2%). Attempted sublimation (4 hr, 100° (0.15 mm)) failed to transfer any material to the cold finger.

Low-Temperature Photolysis of the Sodium Salt of 5H-Dibenzo[a,c]cyclohepten-5-one Tosylhydrazone in the Presence of Dimethyl Fumarate. 5H-Dibenzo[a,c]cyclohepten-5-one tosylhydrazone sodium salt (0.212 g, 0.538 mmol) was photolyzed 1.5 hr at −60° in 30 ml of a saturated, dry tetrahydrofuran solution of dimethyl fumarate (2.60 g, 18.0 mmol, recrystallized from chloroform–hexane). The solution was allowed to come to room temperature and suction filtered. The solvent was removed and dimethyl fumarate sublimed away at 40° (0.2 mm) overnight. The ¹H nmr spectrum of the residue showed no vinyl protons to a limit of detection of ∼2% and was similar to that of the reaction mixture obtained on photolysis in the absence of dimethyl fumarate; tlc, also, gave no indication of dimethyl fumarate reaction products.

Pyrolysis of 5H-Dibenzo[a,c]cyclohepten-5-one Tosylhydrazone Sodium Salt in the Presence of 2,3,4,5-Tetraphenylcyclopentadienone. 5H-Dibenzo[a,c]cyclohepten-5-one sodium salt (0.32 g, 0.80 mmol) and 2,3,4,5-tetraphenylcyclopentadienone (1.00 g, 2.6 mmol) were dissolved in 15 ml of dry tetrahydrofuran and stirred rapidly at 110 ± 5° for 3.5 hr in a 3 oz Fisher-Porter Aerosol Compatibility Tube. The tube was cooled to room temperature and propiolic acid (1.09 g, 15.6 mmol) added, and the mixture was reheated in the sealed tube at 110 ± 5° for 80 min and then cooled

and diluted with 50 ml of toluene. Sodium carbonate was added. The mixture was stirred 4 hr and filtered. Solvent was removed, and preparative layer chromatography (cyclohexane–benzene, 2:1, three elutions) permitted isolation of the principal product as the only major band that moved up the plate (fastest moving band, intense blue fluorescence under uv light). The product, 10,11,12,13-tetraphenyl-9H-cyclohepta[l]phenanthrene (27) (0.218 g, 0.40 mmol, 50% yield), crystallized as a white powder contaminated with a trace of 9,10,11,12-tetraphenyl-11H-cyclohepta[l]phenanthrene or perhaps 9,10,11,12-tetraphenyl-9H-cyclohepta[l]phenanthrene (^{1}H nmr (CDCl$_3$): τ 4.52 (bs, methine, H)). Recrystallization from benzene–pentane gave pure 27 (0.167 g, 0.31 mmol, 38% yield) with the following properties: mp 214–215°; uv, λ_{max} (CH$_3$CN) 357 nm (ϵ 1,300), 338 (sh, 3,200), 272 (sh, 42,000), 257 (60,000); ir (KBr) 3080, 3060, 3020, 1600, 1490, 1440, 1075, 1020, 910, 755, 720, 700 cm^{-1}; ^{1}H nmr (CDCl$_3$) τ 1.25–1.6 (m, 2 H), 1.85–2.25 (m, 2 H), 2.4–2.9 (m, 4 H), 3.09 (bs, 20 H), 5.38 (d, $J = 12.5$ Hz, 1 H), 6.08 (d, $J = 12.5$ Hz, 1 H); mass spectrum, m/e 546 (M$^+$, 100), 469 (17), 455 (13), 392 (26), 369 (45), 292 (14), 290 (19).

Anal. Calcd for C$_{43}$H$_{30}$: C, 94.47; H, 5.53. Found: C, 94.27; H, 5.67.

Thermal Rearrangement of 10,11,12,13-Tetraphenyl-9H-cyclohepta[l]phenanthrene (27). 10,11,12,13-Tetraphenyl-9H-cyclohepta-[l]phenanthrene (27) (0.07 g, 0.13 mmol) was dissolved in 0.5 ml of tetrachloroethylene and placed in an nmr tube. Nmr spectra were taken as the temperature was gradually increased. No change in the spectrum occurred until the temperature reached 150°. Heating at 160° for 1 hr caused the doublet of doublets (τ 5.38 and 6.08, $J = 12.5$ Hz) to lose resolution and broad humps to appear in the same region of the spectrum. On cooling the nmr spectrum showed the doublets due to 27 along with the broad singlet (τ 4.52) due to an H-shift isomer and totally aromatic material. Preparative layer chromatography (cyclohexane–benzene, 2:1, three elutions) failed to separate the components. Recrystallization from chloroform also failed to give a pure product. The mass spectrum of the mixture had a parent ion at 546 of more than five times the intensity of any other fragment, and a mp 297–299° was recorded.

Low-Temperature Photolysis of 5H-Dibenzo[a,c]cyclohepten-5-one Tosylhydrazone Sodium Salt in the Presence of 1,3-Cyclopentadiene. 5H-Dibenzo[a,c]cyclohepten-5-one tosylhydrazone sodium salt (0.20 g, 0.50 mmol) was photolyzed 40 min at −60° in 20 ml of dry tetrahydrofuran containing freshly prepared cyclopentadiene monomer[57] (5 ml, 75 mmol). The reaction mixture was allowed to warm to 5°, and solvent was removed under reduced pressure. (The last trace of dicyclopentadiene was removed *in vacuo*.) The residue was taken up in cyclohexane and column chromatographed on silica gel (cyclohexane). A single component, *endo*-2,3-(*o*-biphenylenyl)tricyclo[3.2.1.0^{2,4}]oct-6-ene (18) (0.094 g, 0.37 mmol, 73% yield), eluted from the column. Molecular distillation (110° (0.2 mm)) yielded a pure, colorless liquid with the following properties: uv, λ_{max} (isooctane), 308 (ϵ 2,300), 273 (4,700), 257 (5,100), 248 (7,700), 239 (8,200), 221 (14,000); ir (film) 3060, 3030, 2970, 2930, 2860, 1600, 1490, 1445, 1330, 1245, 1045, 1020, 890, 850, 790, 745, 740, 725, 695, 675, 620 cm^{-1}; ^{1}H nmr (CCl$_4$) τ 2.0–2.3 (m, 2 H), 2.4–2.7 (m, 2 H), 2.75–3.05 (m, 4 H), 3.95 (*ca.* t, 2 H), 6.61 (bs, H1, 1 H), 6.89 (bs, H5, 1 H), 7.49 (d, H3, $J_{3,4} = 2.8$ Hz, 1 H), 7.73 (d, H8, $J_{gem} = 6.8$ Hz, 1 H), 8.10 (d, H8, 1 H), 9.39 (d of doublets, H4, $J_{3,4} = 2.8$ Hz, $J_{4,5} = 2.6$ Hz, 1 H); mass spectrum, m/e 256 (M$^+$, 100), 216 (75), 192 (52).

Anal. Calcd for C$_{20}$H$_{16}$: C, 93.71; H, 6.29. Found: C, 93.50; H, 6.41.

Low-Temperature Photolysis of 5H-Dibenzo[a,c]cyclohepten-5-one Tosylhydrazone Sodium Salt with Subsequent Addition of 1,3-Cyclopentadiene. (a) 5H-Dibenzo[a,c]cyclohepten-5-one tosylhydrazone sodium salt (0.103 g, 0.260 mmol) was placed in 25 ml of dry tetrahydrofuran. The solution was cooled to −60° and photolyzed 7 min with rapid stirring. The light was extinguished, and 1,3-cyclopentadiene (7 ml, 100 mmol) at −78° was added within 3 sec. The solution was allowed to warm to 5°, and solvent was partially removed under reduced pressure. The solution was filtered, and the remainder of the solvent was evaporated (the last trace of dicyclopentadiene being removed under hard vacuum). The cyclopentadiene adduct 18 was isolated by preparative layer chromatography (pentane, three elutions) side-by-side with authentic material on the same plate. An ultraviolet spectrum in isooctane established the presence of 18 (0.0031 g, 0.012 mmol, 4.7% yield).

(b) In an identical experiment, 1,3-cyclopentadiene was added 125 sec after photolysis ceased. An equivalent work-up and quanti-

tative determination by uv spectrophotometry indicated the formation of adduct 18 (0.0024 g, 0.0094 mmol, 3.6% yield).

Low-Temperature Photolysis of 5H-Dibenzo[a,c]cyclohepten-5-one Tosylhydrazone Sodium Salt in the Presence of Furan. (a) 5H-Dibenzo[a,c]cyclohepten-5-one tosylhydrazone sodium salt (0.15 g, 0.38 mmol) was photolyzed 30 min at −60° in a 1:1 by volume solution of dry tetrahydrofuran and furan (freshly distilled from sodium hydroxide) of total volume 25 ml. The reaction mixture was allowed to come to room temperature and filtered. Solvent was removed, and the remaining yellow oil was separated by preparative layer chromatography (benzene, two elutions). The major product, 1,7-(*o*-biphenylenyl)-*endo*-2,5-epoxynorcar-3-ene (19) (0.045 g, 0.18 mmol, 47% yield), was the fourth distinguishable band (just preceding a pale yellow material) on the preparative plate and quenched uv light rather poorly. Recrystallization from benzene–hexane and then from 95% ethanol gave white needles with the following properties: mp 157–158°; uv, λ_{max} (CH$_3$CN) 307 nm (ϵ 3,400), 268 (sh, 14,300), 234 (30,600); ir (KBr) 3060, 3030, 1490, 1450, 1435, 1045, 1000, 970, 760, 745, 730, 620, 575 cm^{-1}; ^{1}H nmr (CDCl$_3$) τ 1.9–2.15 (m, 2 H), 2.4–3.0 (m, 7 H), 3.35–3.55 (d of doublets, 1 H), 4.98 (d of doublets, 2 H), 6.39 (d, $J_{6,7} = 2.6$ Hz, 1 H), 9.60 (d, $J_{6,7} = 2.6$ Hz, 1 H); Table 1 lists ^{1}H nmr (CDCl$_3$)

Table I. Effect of Added Shift Reagent on ^{1}H Nmr Spectra of Adduct 19

Mole ratio Eu-(fod)$_3$:44	Hz downfield from TMS at 100.1 MHz					
	H2	H3	H4	H5	H6	H7
0.0	506	707	652	499	40	361
0.2	1197	954	914	1187	349	1149
0.4	1739	1153	1118	1674	582	1760
0.6	2180	1322	1286	1980	744	2220

as a function of the mole ratio of Eu(fod)$_3$ added (nonaromatic protons only, 0.035 g of 19 in 0.5 ml of CDCl$_3$); mass spectrum, m/e 258 (M$^+$) (low temperature required or the M$^+$ peak disappears and one at 380 appears).

Anal. Calcd for C$_{19}$H$_{14}$O: C, 88.34; H, 5.46. Found: C, 88.27; H, 5.51.

(b) Room-temperature photolysis of 5H-dibenzo[a,c]cyclohepten-5-one tosylhydrazone sodium salt (0.143 g, 0.36 mmol) in a 1:1 by volume tetrahydrofuran–furan solution (40 ml) for 15 min with other conditions and work-up identical with those employed in the low-temperature photolysis experiment yielded adduct 19 (0.040 g, 0.15 mmol, 43% yield) as the major product. Physical and spectral properties were as reported for the material formed on low-temperature photolysis.

(c) Room-temperature photolysis of 5H-dibenzo[a,c]cyclohepten-5-one tosylhydrazone sodium salt (0.117 g, 0.30 mmol) in 25 ml of 1:1 by volume tetrahydrofuran–furan for 50 min with conditions and work-up identical with those of (b) above gave 1.7-(*o*-biphenyl-enyl)-*endo*-2,5-epoxynorcar-3-ene (19) (0.004 g, 0.015 mmol, 5% yield) as a minor product.

(d) Pyrolysis of 5H-dibenzo[a,c]cyclohepten-5-one tosylhydrazone sodium salt (0.10 g, 0.25 mmol) was carried out at 115° in 15 ml of furan for 30 min. The reaction mixture was cooled and suction filtered. Furan was evaporated. Adduct 19 (0.0072 g, 0.028 mmol, 11% yield) was isolated by preparative layer chromatography (benzene, two elutions) as a minor product and was identical by tlc, uv, and ^{1}H nmr with material previously obtained. There was no indication of any exo-epoxy isomer.

Low-Temperature Photolysis of 4,5-Benzotropone Tosylhydrazone Sodium Salt in the Presence of 1,3-Cyclopentadiene. 4,5-Benzotropone tosylhydrazone sodium salt[1] (0.256 g, 0.74 mmol) was photolyzed 75 min at −60° in 20 ml of dry tetrahydrofuran containing 1,3-cyclopentadiene monomer[52] (7 ml, 100 mmol, transferred at −78°). The reaction mixture was allowed to warm to 5°, and solvent and cyclopentadiene were removed under reduced pressure. The residue was taken up in cyclohexane and passed through an alumina column (grade lll) to remove sodium toluenesulfinate and a very slightly soluble red material that seemed to be the major product. Solvent removal left the hydrocarbon products (0.038 g), mainly *endo*-5,6-benzotetracyclo[7.2.1.0^{2,7}.0^{2,8}]-dodeca-3,5,10-triene (22) and a number of minor components that appeared (nmr) to be secondary photolysis products and naphthylcarbene addition and insertion products. Preparative layer chro-

matography (pentane, three elutions, the leading band isolated) followed by molecular distillation (90° (0.15 mm)) gave a colorless liquid (0.025 g, 0.12 mmol, 16% yield) with the following properties: ir (film) 3060, 3020, 2970, 2930, 2860, 1485, 1455, 1330, 1235, 1040, 1025, 1000, 895, 860, 840, 785, 770, 755, 740, 730, 625 cm^{-1}; ^{1}H nmr (CDCl$_3$) τ 2.65–2.95 (m, 4 H), 3.71 (narrow AB pattern, 2 H), 3.9–4.25 (m, 2 H), 6.93 (bs, 1 H), 7.05 (bs, 1 H), 7.52 (d, $J_{7,8}$ = 2.8 Hz, 1 H), 7.75–8.0 (m, J_{gem} = 6.8 Hz, 1 H), 8.18 (d, J_{gem} = 6.8 Hz, 1 H), 9.65 (narrow d of doublets, $J_{7,8}$ = 2.8 Hz, $J_{8,9}$ = 2.6 Hz, 1 H); mass spectrum, m/e 206 (M$^+$, 100), 178 (54), 165 (69); exact mass 206.1091 (calcd for C$_{16}$H$_{14}$, 206.1095).

Pyrolysis of 4,5-Benzotropone Tosylhydrazone Sodium Salt in the Presence of 2,3,4,5-Tetraphenylcyclopentadienone. 4,5-Benzotropone tosylhydrazone sodium salt (0.36 g, 1.05 mmol) and 2,3,4,5-tetraphenylcyclopentadienone (1.0 g, 2.6 mmol) were dissolved in 15 ml of dry tetrahydrofuran and stirred rapidly at 115 ± 5° for 2 hr in a sealed tube under nitrogen. Solvent was removed under reduced pressure, and the reaction products were dissolved in 50 ml of toluene. Propiolic acid (1.0 g, 14 mmol) was added and the solution heated at reflux for 30 min (until the tetracyclone color lightened). The solution was cooled, and an excess of sodium carbonate added. After stirring 30 min, the mixture was filtered through Celite 545. Solvent was removed under reduced pressure, and the residue was twice subjected to preparative layer chromatography (benzene–carbon tetrachloride–pentane, 1:1:1, three elutions). Three products were obtained. 7,8,9,10-Tetraphenyl-9H-cyclohepta[a]naphthalene (28) (0.046 g, 0.093 mmol, 9% yield) was the fastest moving component and had a bright blue fluorescence under uv light. It was recrystallized from benzene–pentane as a colorless solid with the following properties: mp 212–213°; uv, λ_{max}(CH$_3$CN) 330 nm (sh, ϵ 13,000), 281 (39,500), 240 (41,000); ir (KBr) 3060, 3010, 2920, 1600, 1495, 1445, 1080, 1035, 820, 770, 700, 600, 550, 530 cm^{-1}; ^{1}H nmr (CDCl$_3$) τ 1.6–1.9 (m, 1 H), 2.21 (bs, 1 H), 2.3–3.3 (m, 25 H), 4.57 (bs, 1 H); mass spectrum, m/e 496 (M$^+$, 100), 419 (17), 406 (10), 342 (59); exact mass 496.2143 (calcd for C$_{39}$H$_{28}$, 496.2191). The second component on the plate (0.160 g, 0.305 mmol, 29% yield) was tentatively identified as 6α,11α-dihydro-7,8,9,10-tetraphenylbenzo[a]naphtho[2,1-d]furan from the following spectral properties after a recrystallization from benzene–pentane: mp 275–277°; uv, λ_{max}(CH$_3$CN) 300 nm (ϵ 6,800), 243 (45,000); ir (KBr) 3060, 3030, 2910, 1600, 1565, 1495, 1445, 1400, 1295, 1210, 1160, 1075, 1030, 940, 915, 830, 795, 755, 700, 660, 600, 560, 545 cm^{-1}; ^{1}H nmr (CDCl$_3$) τ 2.5–3.0 (m, 9 H), 3.20 (bs, 15 H), 3.69 (d of doublets, $J_{5,6}$ = 9 Hz, $J_{5,6a}$ = 2.5 Hz, 1 H), 4.24 (d, $J_{6a,11a}$ = 9 Hz, 1 H), 4.76 (d of doublets, $J_{5,6}$ = 9 Hz, $J_{6,6a}$ = 3 Hz, 1 H), 5.58 (d of triplets, $J_{6a,11a}$ = 9 Hz, $J_{5,6a}$ = $J_{6,6a}$ = 2.5–3 Hz, 1 H); mass spectrum, m/e 524 (M$^+$).

Anal. Calcd for C$_{40}$H$_{28}$O: C, 91.57; H, 5.38. Found: C, 91.25; H, 5.40.

The third product with the smallest R_f value was β-naphthyltetraphenylphenol (0.094 g, 0.18 mmol, 17% yield). The optimum yield of the phenol may not have been obtained since work-up conditions could have removed a portion of this product. The crude material became bright orange in the presence of sodium hydroxide and an nmr signal at τ 4.78 was removed by shaking with deuterium oxide. Recrystallization from ethanol–water gave pure phenol with the following properties: mp 235–237°; ir (KBr) 3530, 3050, 3020, 1600, 1500, 1440, 1400, 1290, 1270, 1200, 1135, 1105, 1070, 750, 725, 700, 600, 480 cm^{-1}; ^{1}H nmr (CDCl$_3$) τ 2.2–2.9 (m, 12 H), 3.2 (d, 15 H), 4.78 (s, 1 H); mass spectrum, m/e 524 (M$^+$).

Anal. Calcd for C$_{40}$H$_{28}$O: C, 91.57; H, 5.38. Found: C, 91.39; H, 5.42.

Thermolysis of the three products, each in separate sealed tubes at 115 ± 5° in tetrahydrofuran for 2 hr, failed to convert any compound to any other.

Low-Temperature Photolysis of 3,4-Benzotropone Tosylhydrazone Sodium Salt in the Presence of 1,3-Butadiene. 4,5-Benzotropone tosylhydrazone sodium salt (0.228 g, 0.66 mmol) in 15 ml of dry tetrahydrofuran was cooled to −60° in the photolysis cell. An equal volume of 1,3-butadiene was condensed into the cell, and photolysis was carried out for 2 hr. The reaction mixture was warmed to room temperature under a stream of nitrogen as the

butadiene evaporated. The solution was further reduced in volume at 25° under reduced pressure and filtered through magnesium sulfate (anhydrous) to remove sodium toluenesulfinate and an amorphous red solid that precipitated. Preparative layer chromatography (pentane, three elutions) permitted the isolation of two C$_{15}$ isomers. The leading component, 4,5-benzotricyclo[5.4.0.0^{1,6}]undeca-2,4,9-triene (24) (0.014 g, 0.072 mmol, 11% yield), was obtained after molecular distillation (70° (0.15 mm)) as a colorless liquid with the following properties: uv, λ_{max}(isooctane) 308 nm (sh, ϵ 1,600), 276 (6,050), 223 (22,000); ir (film) 3020, 2890, 2830, 1485, 1455, 1435, 1220, 1115, 1055, 980, 795, 780, 765, 750, 725, 670, 645 cm^{-1}; ^{1}H nmr (CDCl$_3$) τ 2.6–3.0 (m, 4 H), 3.85 (AB pattern, 2 H), 4.35–4.55 (m, 2 H), 7.47 (bs, 4 H), 7.64 (d, $J_{6,7}$ = 4.7 Hz, 1 H), 9.45–9.75 (m, 1 H); mass spectrum, m/e 194 (M$^+$, 22), 179 (27), 141 (89), 140 (100), 125 (34); exact mass 194.108 (calcd for C$_{15}$H$_{14}$, 194.1095).

Anal. Calcd for C$_{15}$H$_{14}$: C, 92.74; H, 7.26. Found: C, 92.64; H, 7.28.

The trailing component was highly contaminated with impurities, but an additional preparative layer chromatography (pentane, five elutions) permitted isolation of 1-vinyl-6,7-benzospiro[2.6]-nona-4,6,8-triene (23) (0.003 g, 0.016 mmol, 3% yield) by judicious removal of the center portion of a broad band of poorly separated compounds. After molecular distillation (70° (0.15 mm)) this spiro compound 23 had the following properties: ir (film) 3060, 3020, 1630, 1490, 1440, 1155, 1040, 990, 940, 900, 810, 760, 745, 705 cm^{-1}; ^{1}H nmr (CDCl$_3$) τ 2.96 (s, 4 H), 3.72 (d, $J_{4,5}$ = 11.5 Hz, 1 H), 3.84 (d, $J_{8,9}$ = 11.5 Hz, 1 H), 4.2–4.8 (m, 1 H), 4.75–5.2 (m, 3 H), 8.25–9.2 (m, 3 H); mass spectrum, m/e 194 (M$^+$, 73), 179 (100), 178 (62), 165 (45), 128 (96), exact mass 194.1085 (calcd for C$_{15}$H$_{14}$, 194.1095).

Low-Temperature Photolysis of 1-Vinyl-6,7-benzospiro[2.6]nona-4,6,8-triene (23). In the small volume photolysis cell (Pyrex) employing the standard conditions for low-temperature formation of aromatic carbenes from tosylhydrazone salts, 1-vinyl-6,7-benzospiro[2.6]nona-4,6,8-triene (0.002 g, 0.01 mmol) was photolyzed 1 hr at −60° in 20 ml of dry tetrahydrofuran. Solvent removal followed by preparative layer chromatography (pentane/5% benzene) gave approximately 75% recovery of starting material along with trace amounts of two other materials neither of which was 4,5-benzotricyclo[5.4.0.0^{1,6}]undeca-2,4,9-triene (24) as determined by tlc and uv. No trace of 24 could be detected by uv spectrophotometry when that portion of the preparative layer chromatography plate expected to contain this compound (chromatographed side-by-side with an authentic sample on the same plate) was extracted. The limit of detection by uv was better than 2 × 10^{-5} g (1%).

Generation of Phenanthrylcarbene (15) in the Presence of Furan. (a) Phenanthrene-9-carboxaldehyde tosylhydrazone sodium salt (0.15 g, 0.63 mmol) was photolyzed 1.5 hr at −60° in a 1:1 by volume solution of tetrahydrofuran–furan of total volume 30 ml. The reaction mixture was allowed to come to room temperature and filtered. Solvent was removed, and the residue was inspected by ^{1}H nmr spectroscopy. There was no indication of the formation of any 1,7-(o-biphenylenyl)-endo-2,5-epoxynorcar-3-ene (19). Preparative layer chromatography (benzene, two elutions) side-by-side with authentic 19 on the same plate, extraction of the portion of the plate expected to contain 19, and analysis by uv spectrophotometry failed to indicate the presence of the adduct to a limit of detection of better than 2 × 10^{-4} g (0.1% yield).

(b) Phenanthrene-9-carboxaldehyde tosylhydrazone sodium salt (0.50 g, 1.26 mmol) was pyrolyzed in 20 ml of neat furan (sealed tube) for 1 hr at 115 ± 5° with rapid stirring. The reaction mixture was cooled to room temperature and filtered. Solvent was removed. No trace of adduct 19 could be detected in the ^{1}H nmr spectrum of the residue or by tlc.