References and Notes

(1) It is established in the solvolysis of other phosphorus derivatives. (a) For general remarks, see: M. J. Gallagher and I. D. Jenkins, *Top. Stereochem.* **3**, Chapter 1 (1968). (b) For enzymatic solvolysis of cyclic phosphorothioates: W. Saenger, *Angew. Chem., Int. Ed. Engl.*, **12**, 591 (1973); D. A. Usher, D. I. Richardson, Jr., and F. Eckstein, *Nature (London)*, **228**, 663 (1970). (c) For nucleophilic substitution of chiral phosphorothioate: M. Mikolajczyk, J. Omelanczyk, and M. Para, *Tetrahedron*, **28**, 3855 (1972); J. Michalski and M. Mikolajczyk, *Chem. Ind. (London)*, 661 (1964). (d) For solvolysis of chiral phosphinamides: T. Koizumi, Y. Kobayashi, and E. Yoshii, *J. Chem. Soc., Chem. Commun.*, 678 (1974); *Chem. Pharm. Bull.*, **24**, 834 (1976).

(2) N. P. B. Dudman and B. Zerner, *J. Am. Chem. Soc.*, **95**, 3019 (1973).

(3) (a) C. R. Hall, T. D. Inch, G. J. Lewis, and R. A. Chittenden, *J. Chem. Soc., Chem. Commun.*, 720 (1975); (b) D. B. Cooper, C. R. Hall, and T. D. Inch, *ibid.*, 721 (1975); (c) D. B. Cooper, J. M. Harrison, and T. D. Inch, *Tetrahedron Lett.*, 2697 (1974); (d) J. M. Harrison, T. D. Inch, and G. J. Lewis, *J. Chem. Soc., Perkin Trans. 1*, 1892 (1975).

(4) In the case of ref 3a, several steps were required to secure the sugar moiety.

(5) It seems rather difficult to prepare dialkyl aryl phosphates by this method because the P–OAr bond is very labile to alkaline conditions.

(6) The use of L-proline derivatives for the asymmetric synthesis of chiral carbon compounds has been extensively studied by S.-I. Yamada and his collaborators: S.-I. Yamada, K. Hiroi, and K. Achiwa, *Tetrahedron Lett.*, 4233 (1969); S.-I. Yamada, and G. Otani, *ibid.*, 4237 (1969); 1133 (1971); K. Hiroi, K. Achiwa, and S.-I. Yamada, *Chem. Pharm. Bull.*, **20**, 246 (1972); K. Hiroi and S.-I. Yamada, *ibid.*, **23**, 1103 (1975); T. Sone, S. Terashima, and S.-I. Yamada, *ibid.*, **24**, 1273, 1288 (1976).

(7) The reaction was carried out at room temperature for 3–4 h.

(8) The reaction was carried out at room temperature for 8–12 h.

(9) All new compounds gave satisfactory elemental analyses and spectral data.

(10) Yields are based on phenyl phosphorodichloridate in the case of **3a**, **3b**, **4a**, and **4b**.

(11) All distillations were performed with a short-path distillation apparatus and bath temperatures are described.

(12) All $[\alpha]_D$ measurements were taken in carbon tetrachloride solution.

(13) The alcoholysis was performed with 0.4–1.0 mmol of the phosphoramidate in 4–10 mL of 1 M H_2SO_4–alcohol for 4 h.

(14) The reaction mixture was diluted with H_2O and extracted with Et_2O. After washings with dilute HCl, H_2O, dilute $NaHCO_3$, and H_2O there was obtained almost pure oily dialkyl phenyl phosphate, which was subjected to microdistillation.

(15) The enantiomeric purities of methyl ethyl phenyl phosphate and methyl *n*-butyl phenyl phosphate were determined as >97% according to Hall's method (ref 3a and 3b). When a twofold excess of $Eu(hfc)_3$ was added to a carbon tetrachloride solution of each enantiomer, only one P–OMe doublet was observed, whereas a pair of doublets was detected with a mixture (3:97) of enantiomers. Since the acid-catalyzed alcoholysis of phosphoramidate (**3** and **4**) should proceed through A-2 mechanism, other dialkyl phenyl phosphates are considered to possess a comparable degree of optical purity. The observed differences in $[\alpha]_D$ could be attributable to some experimental errors.

(16) Reaction conditions (temperature, acids, and acid concentration) and workup procedure for obtaining maximum yields are being investigated.

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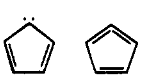
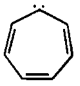
4,5-Benzo-1,2,4,6-cycloheptatetraene

Summary: 4,5-Benzo-1,2,4,6-cycloheptatetraene and one of its methyl derivatives have been generated by the dehydrohalogenation of benzohalocycloheptatrienes.

Sir: Cyclic, fully conjugated carbenes have been the subject of considerable research interest.[1] In principle, valence isomeric allene structures can be postulated for each of the carbenes. While there has been no need to invoke an allenic isomer of cyclopentadienylidene, the situation has not been as clear with cycloheptatrienylidene.[2] The chemistry of the C_7H_6 intermediate generated from the photolysis or thermolysis of the sodium salt of tropone tosylhydrazone has been logically interpreted in terms of **1**.[3] The intermediate shows low reactivity with electron-rich alkenes[3a] and a positive ρ value in its addition to substituted styrenes.[3b] These properties are consistent with extended Hückel calculations which predict **1** to be a relatively nucleophilic carbene in its lowest energy singlet state.[4] Untch's report of the dehydrochlorination of 1-chloro-1,3,5-cycloheptatriene[5] generated interest in the cycloheptatetraene **2**, since the product, heptafulvalene, had previously been isolated from reactions where the intermediacy of **1** had been implicated.[3] The possibility that **2** might be involved in the reactions of **1** was increased when Jones, Sabin, and co-workers reported the results of INDO calculations which concluded that **2** (nonplanar) was more stable than **1** (planar) by 14 kcal/mol.[6,7] These calculations also indicated that the appropriate benzo annelation of the seven-membered ring would further stabilize the allene form (**4**) relative to its carbene analogue (**3**). In this paper, we wish to report the generation of **4** and one of its methyl derivatives.





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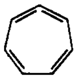

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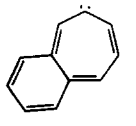

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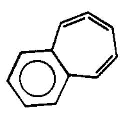

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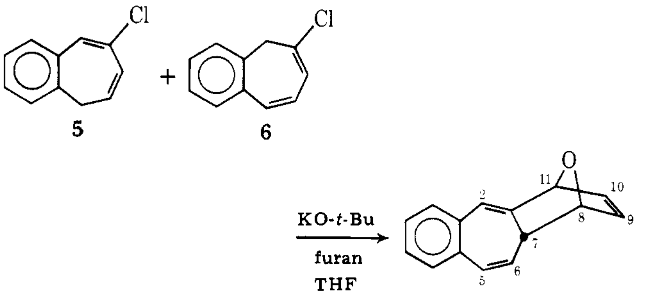
When a mixture of **5** and **6**[8,9] was treated with potassium *tert*-butoxide (KO-*t*-Bu) in tetrahydrofuran (THF), a rapid, slightly exothermic reaction produced a golden polymer (81%).[10] When the reaction was carried out in the presence of excess furan, the adduct **7** was isolated (21%) along with some polymer. The use of $Eu(dpm)_3$ as a chemical shift reagent aided in the structure assignment of **7**.[11]



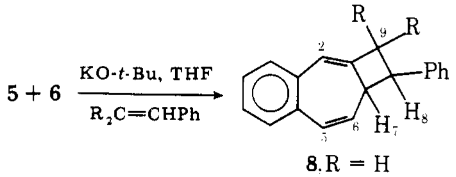
5 6 7

When the reaction was conducted in the presence of excess styrene, **8** was formed in 35% yield. The structure proof for **8** rests on its normal and decoupled NMR spectra and the analogous spectra for **9**, which was prepared by using β,β'-

Table I. NMR Data for 8 and 9 (CCl_4, Me_4Si, δ)

	H_2 and H_5	H_6	H_7	H_8	H_9, $H_{9'}$	H_{arom}
8	6.1–6.5 (m, 2 H)	5.62 (d of d, 11.8 and 2.0 Hz)	3.95 (br m, 1H)	3.2–3.8 (m, 1 H)	2.8–3.2 (m, 2 H)	7.2 and 7.4 (br s, 9 H)
9[a]	6.2–6.5 (m, 2 H)	5.62 (d of d, 11.8 and 2.0 Hz)	3.95 (d of m, 8.8 Hz)	3.49 (br d, 8.8 Hz)		7.2 and 7.4 (br s, 9 H total)

[a] When H_7 of **9** is irradiated in a decoupling experiment, H_5 collapses to a doublet (δ 6.32, $J_{5,6}$ = 11.8 Hz) and H_2 becomes a singlet (δ 6.26).

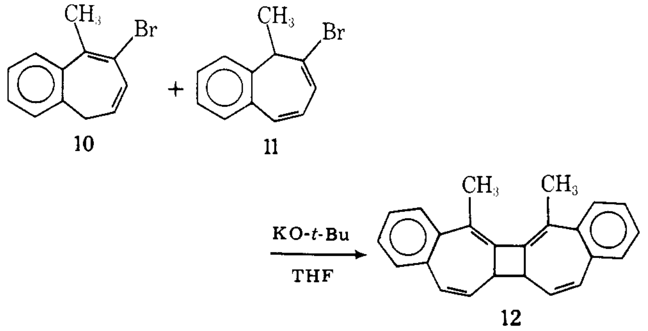


8, R = H

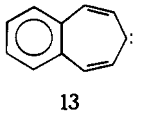
9, R = D

dideuteriostyrene as the trapping reagent.[13] Although the coupling constant between H_7 and H_8 (8.8 Hz) is of such a magnitude to be consistent with either a cis or a trans relationship,[14] a tentative trans arrangement is proposed on the basis of chemical shift evidence.[15]

Although the above intermediate readily underwent polymerization in the absence of trapping reagents, a methyl derivative gave excellent yields of a dimer. Thus, the reaction of KO-*t*-Bu with **10** and **11** at 0 °C gave the head-to-head dimer **12**.[16] Other isomers were not detected by NMR spectroscopy.



The understanding of allene contributions to the chemistry of cyclic, fully conjugated carbenes is emerging.[17] Although mechanisms which involve carbene additions followed by rearrangements can be written for the above reactions, several points favor strained allene additions. First, the calculated relative energies favor **4** over **3** by 46 kcal/mol,[6] a very substantial difference. Secondly, in this base-promoted elimination method, a simple E2 elimination would result initially in either **4** or the doubly excited p^2 carbene state. The loss of halide ion from a delocalized anion would also give the p^2 carbene. Third, the cycloaddition of the intermediate to the electron-rich diene, furan, is not characteristic of nucleophilic, carbocyclic, aromatic carbenes. Finally, at higher temperatures (135–160 °C in diglyme) neither the intermediate derived from **5–6** nor the one from the **10–11** precursor system shows any tendency to undergo a carbene–carbene rearrangement as does **13**.[18] One of the remaining questions, though, concerns the involvement of **2** itself in the chemistry of **1** when generated from the photolysis or thermolysis of the sodium salt of tropone tosylhydrazone.[19]



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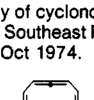
References and Notes

(1) For a review of this area, see H. Dürr, *Top. Curr. Chem.*, **40,** 103 (1973).

(2) Evidence for the intermediacy of cyclononapentaene has been presented: E. E. Waali and N. T. Allison, Southeast Regional American Chemical Society Meeting, Norfolk, Va., Oct 1974.



(3) (a) W. M. Jones and C. L. Ennis, *J. Am. Chem. Soc.*, **91,** 6391 (1969); (b) L. W. Christensen, E. E. Waali, and W. M. Jones, *ibid.*, **94,** 2118 (1972); (c) E. E. Waali and W. M. Jones, *ibid.*, **95,** 8114 (1973).

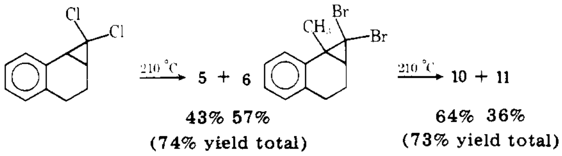
(4) R. Gleiter and R. Hoffmann, *J. Am. Chem. Soc.*, **90,** 5457 (1968).

(5) K. Untch, International Symposium on the Chemistry of Nonbenzenoid Aromatic Hydrocarbon Compounds, Sendai, Japan, August, 1970. We are indebted to Dr. Untch for his private communication of his work.

(6) R. L. Tyner, W. M. Jones, Y. Ohrn, and J. R. Sabin, *J. Am. Chem. Soc.*, **96,** 3765 (1974).

(7) As was pointed out,[6] the calculations do not take into account differences in solvation energies. Since the calculated dipole moment of **1** is significantly greater than that of **2,** the energy difference in solution may be much less than 14 kcal/mol.

(8) The starting halides were prepared by the thermolysis of the following dihalocyclopropanes.



(9) IR and NMR spectra were consistent with the structures proposed for the new compounds. New compounds also gave satisfactory elemental analyses plus mass spectra or satisfactory high resolution mass spectra.

(10) Although the mass spectrum of this material showed a peak at *m/e* 560, appropriate for a tetramer of **4**, its ^{13}C NMR spectrum exhibited an absolute plethora of signals resulting in broad multiplets rather than the usual narrow band spectrum. All attempts to purify the material by column or thin-layer chromatography or by selective extraction failed.

(11) The structure proof for **7** was complex. Several Eu(dpm)$_3$ shifted 60-MHz NMR spectra provided the insight necessary to fully analyze the 100-MHz spectrum of **7.** The 100-MHz spectrum showed doublets of doublets at the following chemical shifts (CCl_4, Me_4Si, δ): 5.05 (10.5 and 3.0 Hz, H_6), 5.07 (1.8 and 1.0 Hz, H_{11}), 5.26 (4.9 and 1.0 Hz, H_8), 6.26 (10.5 and 2.4 Hz, H_5), 6.29 (5.7 and 1.0 Hz, H_9), 6.42 (2.0 and 1.0 Hz, H_2), and 6.74 (5.7 and 1.8 Hz, H_{10}). In addition, H_7 gave a six-line signal with some different spacings at δ 3.53. By using the measured values of $J_{7,8}$ (4.9 Hz), $J_{6,7}$ (3.0 Hz), $J_{5,7}$ (2.4 Hz), and $J_{2,7}$ (2.0 Hz), the H_7 pattern was calculated. The result was a six-line pattern which corresponded with the observed pattern. The aromatic resonances were found as a multiplet at δ 6.9–7.4.

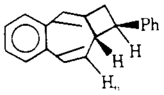
The endo configuration was chosen for **7** on the basis of the agreement factors which were calculated[12] for the endo and exo isomers. Dreiding models were used for the manual measurement of angles and distances. Several 60-MHz spectra using various Eu(dpm)$_3$/**7** ratios were required to resolve each of the nonaromatic resonances in **7.** At Eu(dpm)$_3$/**7** ratios of 0.0725, 0.141, 0.170, and 0.478, agreement factors for the endo isomer (and exo isomer) were 0.095 (0.214), and 0.086 (0.170), 0.066 (0.105), and 0.079 (0.179), respectively.

(12) M. R. Willcott III, R. E. Lenkinski, and R. E. Davis, *J. Am. Chem. Soc.*, **94,** 1742 (1972).

(13) See Table I for NMR data for **8** and **9.**

(14) I. Fleming and D. H. Williams, *Tetrahedron*, **23,** 2747 (1967).

(15) A slight impurity (~5%) in the NMR spectrum of **8** is probably due to its geometric isomer. H_6 in the major isomer appears as a doublet of doublets (11.8 and 2.0 Hz) at δ 5.62. The impurity shows a similar doublet of doublets at δ 4.85. A Dreiding model shows that if the phenyl group is cis to C_6 it should suffer restricted rotation and H_6 would be held in the shielding region of the phenyl ring. Thus, the tentative assignment of **8a** as the predominant isomer.



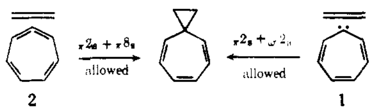
8a

(16) NMR data for **12** (CCl_4): δ 2.36 (s, 6 H, methyl), 3.39 (broadened s, 2 H, methine), 5.84 (d, 11 Hz, 2 H, olefinic β to arom ring), 6.37 (d, 11 Hz, 2 H, olefinic α to arom ring), 7.0–7.6 (m, 8 H, arom). The configuration of the ring fusion is not known.

(17) In a methanoannulene series, Jones and co-workers have shown that the nature of the intermediate is controlled by the position of the carbene carbon (or the central allene carbon): R. A. LaBar and W. M. Jones, *J. Am. Chem. Soc.*, **96,** 3645 (1974); **95,** 2359 (1973); P. H. Gebert, R. W. King, R. A. La Bar, and W. M. Jones, *ibid.*, **95,** 2357 (1973).

(18) W. M. Jones, R. C. Joines, J. A. Meyers, T. Mitsuhashi, K. E. Krajca, E. E. Waali, T. L. Davis, and A. B. Turner, *J. Am. Chem. Soc.*, **95,** 826 (1973).

(19) Viewing the π system in **2** as a conjugated tetraene with both termini sharing



the same carbon (C_2), a thermally allowed $_{\pi}2_s + {}_{\pi}8_s$ cycloaddition giving cyclopropane products is conceivable.

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