# Synthesis and Study of Pseudoaromatic Compounds.
I.   The Synthesis of 8-Vinylheptafulvene

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8-Vinylheptafulvene has been synthesized and by comparison of its n.m.r. and infrared spectra with those of heptafulvalene, 8,8-dicyanoheptafulvene, and tropone, it is concluded that dipolar resonance interactions are not of major importance in the ground state.

Heptafulvene (1a) has aroused considerable theoretical interest because of its close analogy to tropone[2] which suggests that dipolar resonance interaction in the ground state might lead to aromatic character. Molecular orbital and valence bond calculations based on a regular heptagonal ring agree qualitatively with this supposition, predicting a high delocalization energy

1a, X=H
1b, X=CN
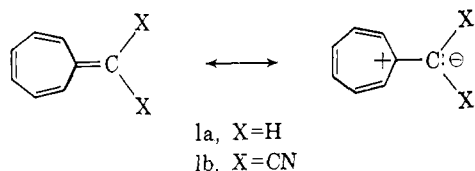
for heptafulvene,[3-5] while recent calculations including bond alternation predict lower delocalization energies.[6,7] Simple MO calculations predict a high dipole moment (4.6 D.)[3] with the ring positive and more refined calculations predict a smaller dipole moment (0.85 D.)[4] in the same direction. However, SCF–MO calculations predict a small dipole moment (0.14 D.)[5] in the opposite direction. The molecular orbital calculations allowing for bond alternation predict dipole moments of 0.23[6] or 0.63 D.[7] Thus theoretical calculations are at variance as to the importance of dipolar resonance contributions, and to their predictions of delocalization energy for heptafulvene.

The recent synthesis of heptafulvene by Doering and Wiley[8] and subsequent determination of the heat of hydrogenation[9] indicate that the molecule does not possess a high π-electron delocalization energy and that the formation of a double bond at the 7-position of cycloheptatriene, to form a completely conjugated system, results in only a slight increase in π-electron delocalization energy.[8,9]

Since the properties of heptafulvene deviate considerably from those based on theoretical prediction, it appeared worthwhile to study this ring system further in order to gain a more precise indication of its structure. The marked instability of heptafulvene severely limits an investigation of its physical properties and thus has precluded the determination of several

data which might be of use. Several derivatives of heptafulvene, substituted at the 8-position, are known which exhibit enhanced stability over the parent compound.[10,11] However, it cannot be ascertained to what extent derivatives containing cyano or carboalkoxy substituents change the ground state properties of the molecule. Thus, the relatively high dipole moment (3 D.) calculated[12] for heptafulvene on the basis of the known dipole moment of 8.8-dicyanoheptafulvene might be substantially in error owing to the enhancement of dipolar resonance contributions (1b) by the highly stabilizing influence of cyano groups toward a negative charge.[13]

For these reasons it appeared desirable to investigate the possibility of synthesizing a derivative of heptafulvene which would introduce a minimum perturbation on the parent system while conferring sufficient stability to enable the determination of certain properties. It is assumed that a vinyl group at the 8-position does not constitute a severe perturbation on the ground state of heptafulvene owing to the stabilization of dipolar resonance forms. Furthermore, from the n.m.r. spectrum it might be possible to ascertain any tendency for a displacement of π-electron density from the seven-membered ring to the side chain by the presence of an additional conjugated double bond.

7-Allylcycloheptatriene (3) can be readily prepared by the addition of cycloheptatrienyl 7-methyl ether[14] (2) to allylmagnesium chloride. The resulting hydrocarbon reacts rapidly with either triphenylmethylcarbonium fluoroborate or hexachloroantimonate to give the corresponding allyltropenium compound and triphenylmethane.[15] Although the hexachloroantimonate salt (4) could be isolated in pure form, the fluoroborate salt was obtained only as an oil at room temperature. The n.m.r. spectrum was completely consistent with the structure of an allyltropenium ion and showed that no rearrangement to the vinyl tropenium system had occurred.

Because of the insolubility of the allyltropenium hexachloroantimonate salt in both dichloromethane and chloroform, it was found more convenient to use the fluoroborate compound for all subsequent reactions,

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(2) H. J. Dauben, Jr., and H. J. Ringold, J. Am. Chem. Soc., 73, 876 (1951); W. von E. Doering and F. L. Detert, ibid., 73, 876 (1951).
(3) G. Berthier and B. Pullman, Trans. Faraday Soc., 45, 484 (1949).
(4) E. D. Bergmann, E. Fischer, D. Ginsburg, Y. Hirshberg, D. Lauie, M. Mayot, A. Pullman, and B. Pullman, Bull. soc. chim. France, 18, 684 (1951).
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(6) A. Julg, ibid., 59, 757 (1962).
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(10) H. J. Dauben, Jr., and R. B. Medz have reported the synthesis of 8,8-diphenylheptafulvene: Abstracts, 145th National Meeting of the American Chemical Society, New York, N. Y., Sept., 1963, p. 75.
(11) T. Nozoe, T. Makai, A. Sato, and 1. Osaka, Bull. Chem. Soc. Japan, 34, 1384 (1961).
(12) M. Yamakawa, H. Watanabe, T. Mukai, T. Nozoe, and M. Kubo, J. Am. Chem. Soc., 82, 5665 (1960).
(13) Nakajima has indicated that the experimental dipole moment may be in error; see ref. 7.
(14) A. G. Harrison, L. R. Honnem, H. J. Dauben, Jr., and F. P. Lossing, J. Am. Chem. Soc., 82, 5593 (1960).
(15) H. J. Dauben, Jr., F. A. Gadecki, K. M. Harmon, and D. L. Pearson, ibid., 79, 4557 (1957).

Fig. 1.—The n.m.r. spectrum of 8-vinylheptafulvene in carbon tetrachloride with tetramethylsilane as internal reference at 60 Mc. (TMS equal to 10 τ).

even though it could not be isolated in pure form. Addition of a solution of allyltropenium fluoroborate in dichloromethane to a solution of trimethylamine[16] in the same solvent produced an immediate and intense red solution and rapid precipitation of trimethylammonium fluoroborate. Since the allyltropenium fluoroborate could not be isolated in pure form, the compound, which was only slightly soluble in chloro-

form, was prepared in chloroform and washed several times with the same solvent before dissolving in dichloromethane and treatment with trimethylamine. For this reason, the yield of the deprotonation step could not be determined. The solutions thus obtained were stable for several days at room temperature with no apparent change. Concentration of these solutions to ca. 0.05 M with a stream of deoxidized nitrogen, addition of carbon tetrachloride, concentrating again, and finally chromatography over alumina gave solutions free of amine which showed no apparent change upon standing for a few days at room temperature. Further concentration of these solutions by a deoxidized nitrogen stream gave solutions suitable for the determination of the n.m.r. and infrared spectra of the 8-vinylheptafulvene. These more concentrated solutions would slowly polymerize, but were stable for several hours if kept under nitrogen.

The structure of this compound as 8-vinylheptafulvene (5) is demonstrated by its n.m.r. spectrum (Fig. 1) which shows no aliphatic or benzenoid proton absorptions, and by its rapid hydrogenation to n-propylcycloheptane. The structure of the latter hydrogenation product was established by identity of its infrared spectrum with that of an authentic sample of n-propylcycloheptane prepared by the reaction of cycloheptanone with n-propylmagnesium bromide, dehydration of the alcohol, and hydrogenation.

Although 8-vinylheptafulvene is stable in solution, concentration of these solutions, by the above-mentioned method, to an oil and redissolving results in partial polymerization to an insoluble, almost colorless, resin. Thus, the vinyl group does confer a slight enhancement of stability over heptafulvene. Also, solutions of 8-vinylheptafulvene which contained excess dimethyl acetylenedicarboxylate showed no reaction upon standing several days at room temperature, in contrast to heptafulvene, which reacts with this same reagent to give a dihydrodicarbomethoxyazulene.[8]

As is the case for heptafulvene, 8-vinylheptafulvene reacts with acids to form the corresponding substituted tropenium ion (6). Although a stable salt could not be isolated, the structure was confirmed by the n.m.r. spectrum. Solutions of the ion were prepared by extracting a carbon tetrachloride solution of the hydrocarbon with trifluoroacetic acid. The n.m.r. spectrum was consistent with protonation at the terminal vinyl position and consisted of a doublet at 7.78 (3 protons), a broad multiplet at 2.88 (2 protons), and a broad peak at 1.17 τ (6 protons). These values are in good agreement with the τ-values for the methylene, the vinyl, and the seven-membered ring protons of both azulenium ion[17] and heptalenium ion.[18]

The solutions obtained by dissolving 8-vinylheptafulvene in acid were deep red, but the color is probably due to some decomposition. The ultraviolet spectrum of a solution of 8-vinylheptafulvene in concentrated sulfuric acid consists of bands at 368, 263, and 224 mμ[19] in close agreement to the ultraviolet spectrum of azulenium ion, which exhibits bands at 352, 257, and 223 mμ, although the relative intensities are quite different.

Since we were unable to isolate 8-vinylheptafulvene, the ultraviolet spectrum was determined by preparing a known volume of a solution of the hydrocarbon in diethyl ether, withdrawing an aliquot and further diluting to get a solution of satisfactory concentration. The original solution was then catalytically hydrogenated and the resulting solution analyzed by vapor phase chromatography.[20]

Although the vinyl substituent is assumed to be a minor perturbation on the ground state of the heptafulvene nucleus, there is little doubt that the excited state is affected to a larger extent. The ultraviolet spectrum of 8-vinylheptafulvene shows a low intensity broad band at 443 mμ (500) and a sharp intense band at 326 mμ (47,900). These values may be contrasted to the ultraviolet spectrum of heptafulvene (Fig. 2) which

(16) H. J. Dauben, Jr., et al., J. Am. Chem. Soc., **83**, 4657 (1961), and also in ref. 10, have shown this method to be a general and useful method of deprotonation of substituted tropenium ions to give related conjugated hydrocarbons.

(17) S. S. Danyluk and W. G. Schneider, J. Am. Chem. Soc., **82**, 997 (1960).

(18) H. J. Dauben, Jr., and D. J. Bertelli, ibid., **83**, 4657 (1961).

(19) Because of no satisfactory way to determine the concentrations, no ε-values were obtained.

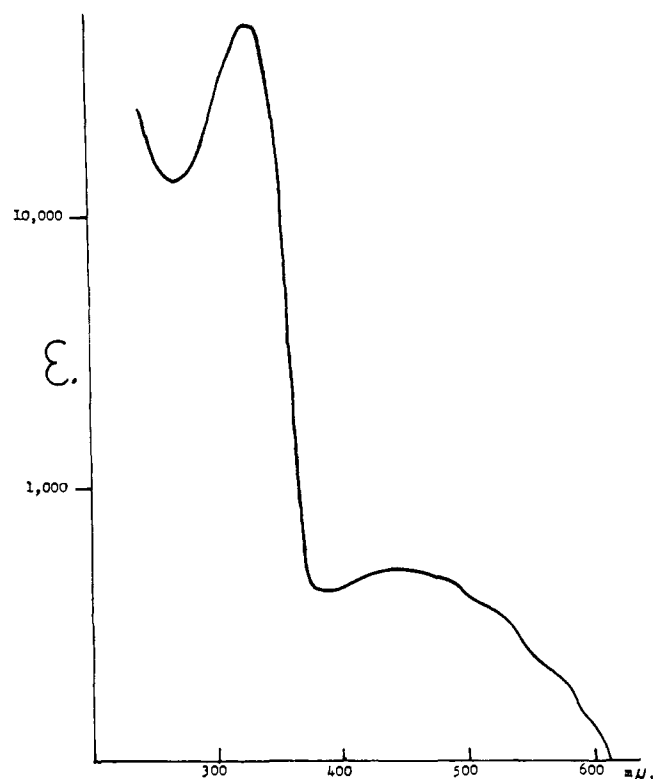(20) This indirect method was also found necessary in the original preparation of heptafulvene; see ref. 8.

Fig. 2.—Ultraviolet spectrum of 8-vinylheptafulvene in diethyl-ether.

shows a low intensity broad band at 427 mµ and a more intense broad band at 279 mµ, a 16- and 47-mµ shift respectively. The bathochromic shift is in the direction expected for both peaks, but the short wave length band is shifted by a greater amount than might be expected. Furthermore, the shape of this latter band is changed considerably, indicating an extensive π-electron interaction of the vinyl group with the heptafulvene nucleus in the excited state. The long wave length band maintains the characteristic shape of the long wave length band of heptafulvene—quite broad and extending far into the visible region.

To facilitate the analysis of the n.m.r. spectrum of 8-vinylheptafulvene, the n.m.r. spectra included in Fig. 3 were also determined. Since both tropone and 8,8-dicyanoheptafulvene (Fig. 3) possess high dipole moments (4.17[21] and 7.49 D.,[12] respectively), and tropone is presumed to exhibit π-electron delocalization,[22] they furnish examples of the chemical shift to be expected for a seven-membered ring system which has important dipolar resonance contributors.[22,23] Also, they should provide an example of the spin–spin splitting pattern to be expected for a delocalized seven-membered ring having six adjacent protons. The n.m.r. spectrum of heptafulvalene[24] should again provide an example of the spin–spin splitting pattern for a seven-membered ring system which is presumed to possess π-electron delocalization, but in which dipolar resonance structures cannot contribute to the n.m.r. chemical shift.

(21) M. Kubo, T. Nozoe, and Y. Kurita, *Nature*, **167**, 688 (1951).

(22) T. Nozoe, "Non-Benzenoid Aromatic Compounds," D. Ginsberg, Ed., Interscience Publishers, Inc., New York, N. Y., 1959, p. 339.

(23) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, p. 279.

(24) J. R. Mayer, Ph.D. Dissertation, Yale University, and W. von E. Doering, "Theoretical Organic Chemistry," The Kekulé Symposium, Butterworths Scientific Publications, London, 1959, p. 35.
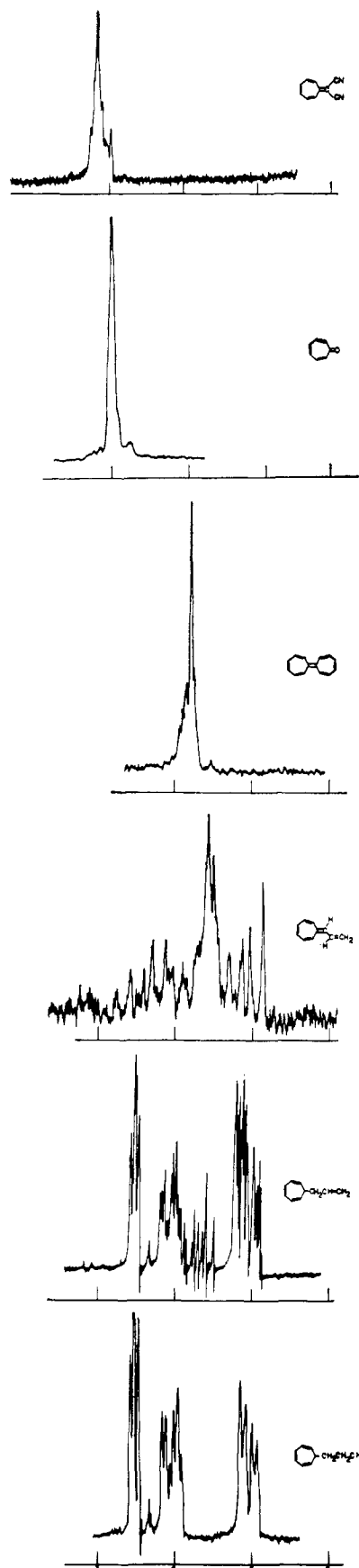
Fig. 3.—The n.m.r. spectra of n-propylcycloheptatriene, allyl-cycloheptatriene, 8-vinylheptafulvene, heptafulvalene, tropone, and 8,8-dicyanoheptafulvene. All spectra were taken in carbon tetrachloride with tetramethylsilane as internal reference (TMS equal to 10 τ) except 8,8-dicyanoheptafulvene which was taken in dimethyl sulfoxide at 60 Mc.

The n.m.r. spectrum of 8,8-dicyanoheptafulvene (Fig. 3) shows a broad multiplet centered at 2.8 τ. The spin-spin splitting pattern indicates an ABC system and that the protons are very nearly equivalent. 8,8-Dicyanoheptafulvene is not sufficiently soluble in carbon tetrachloride to determine the n.m.r. spectrum in that solvent, and dimethyl sulfoxide was used. To ascertain if there was any solvent effect on the chemical shift in dimethyl sulfoxide, the n.m.r. of tropone was also determined in this solvent. The chemical shift of tropone in dimethyl sulfoxide was changed by only 0.05 τ-units from carbon tetrachloride solvent so that the chemical shift value for 8,8-dicyanoheptafulvene is probably reasonably comparable to the remaining chemical shifts in Fig. 2.

The lower τ-values for the protons of both tropone and 8,8-dicyanoheptafulvene are attributed largely to dipolar resonance effects, although inductive effects must be operative to some extent. This assumption is based primarily on the fact that if this lower τ-value were due predominantly to a simple inductive effect, the protons α to the 7-position should be affected to a larger extent than the β- and γ-protons. This latter assumption is borne out by the fact that the α-protons of cycloheptanone are separated from the β- and γ-protons by 0.9 τ-unit.

The n.m.r. spectrum of heptafulvalene again does not exhibit a single peak, but the spin–spin splitting pattern observed indicates an ABC system in which the protons are very nearly identical. The n.m.r. spectrum of dicycloheptatrienyl (dihydroheptafulvalene) is identical in the vinyl region with that of 7-propylcycloheptatriene (Fig. 3), and by comparison it is evident that the removal of two protons from dicycloheptatrienyl to form heptafulvalene results in an extensive alteration in the proton environments making them substantially more equivalent.

The large multiplet centered at *ca.* 4.4 τ in the n.m.r. spectrum of 8-vinylheptafulvene (Fig. 1) appears most reasonably assigned to the ring protons. This assignment is made by analogy to both heptafulvalene and 8,8-dicyanoheptafulvene. Furthermore, integration shows that two protons lie on each side of the larger multiplet. The four peaks at the high-field side centered at *ca.* 4.9 τ are consistent with the pattern expected for the AB part of an ABX system. Since the chemical shift of the terminal vinyl protons should be approximately the same and would be expected to consist of the AB part of an ABX system, this multiplet is assigned to the terminal vinyl protons. The remaining protons on the lowfield side of the large multiplet are then assigned to the 8 and 9 protons, but no distinction is possible between the two.[25]

Subtraction of the vinyl protons of 7-propylcycloheptatriene from those of 7-allylcycloheptatriene allow the assignment of the terminal vinyl protons of 7-allylcycloheptatriene at *ca.* 4.8 τ and the inner vinyl proton at *ca.* 4.3 τ (multiplet centers).[26]

From these data it appears that the terminal vinyl protons shift approximately 0.1 τ-unit upfield comparing 7-allylcycloheptatriene with 8-vinylheptafulvene. The inner vinyl proton has shifted somewhat downfield, but since no definite assignment can be made for this proton in 8-vinylheptafulvene, the extent of this shift cannot be determined precisely. The chemical shift of the ring protons of 8-vinylheptafulvene, being almost identical with that of heptafulvalene, is indicative that there is not an appreciable amount of positive charge in the ring and that dipolar resonance contributors are apparently not of major importance in 8-vinylheptafulvene. This conclusion is substantiated by the small upfield shift of the terminal vinyl protons indicating that some dipolar resonance contribution is present, but that the magnitude is small.

The terminal vinyl carbon–carbon double bond stretching frequency for allylcycloheptatriene appears at 1643 cm.$^{-1}$ in the infrared spectrum and the carbon–hydrogen out-of-plane deformation frequencies appear at 994 and 914 cm.$^{-1}$. The respective frequencies for 8-vinylheptafulvene occur at 1606, 983, and 894 cm.$^{-1}$. The observed shift to lower energies for the carbon–carbon double bond is normal for the change from an isolated to a conjugated vinyl group.[27] The carbon–hydrogen deformation vibrations have been reported to be independent of conjugative effects while being indicative of inductive effects.[27] The shift in the vinyl carbon–hydrogen deformation vibrations in comparing 7-allylcycloheptatriene with 8-vinylheptafulvene are in the direction expected for an electron-releasing substitution effect. These infrared data indicate that a dipolar resonance effect is apparently operative. However, the magnitude of the effect is not large and within the range observed for simple olefins.[27] Thus the infrared data support the n.m.r. data in indicating that dipolar resonance interactions do not contribute substantially to the ground state of 8-vinylheptafulvene.

The small experimental difference in resonance energy between an alkyl cycloheptatriene and heptafulvene (*ca.* 4–6 kcal.) as determined by heat of hydrogenation data,[9] contrasted with the pronounced change in chemical shifts of the ring protons in comparing an alkyl cycloheptatriene with 8-vinylheptafulvene or heptafulvalene, indicates that the n.m.r. chemical shift is highly sensitive to small changes in π-electronic environment. The fact that the ring protons experience a more homogeneous environment in 8-vinylheptafulvene than in 7-allylcycloheptatriene might indicate that the heptafulvene ring is planar or very nearly so in accord with the conclusions of Doering and Wiley.[8] However, this change might also be attributable to the change of the hybridization of the 7-carbon atom from sp^3 to sp^2 which would be expected to shift the 1 and 6 protons downfield. The present data do not allow any definite conclusion concerning this question.

The appearance of the protons of both heptafulvalene and 8-vinylheptafulvene in the olefinic region of the n.m.r. spectrum may be attributed to the fact that neither molecule possesses substantial π-electron delocalization, which is in qualitative agreement with the low experimental stabilization energies of heptafulvalene and heptafulvene.[9]

(25) Although the terminal vinyl protons should exhibit a pattern characteristic of an ABX system, the inner vinyl proton will also couple with the 8 hydrogen. The coupling constants could not be determined because of this additional coupling plus the inability to distinguish between the inner vinyl hydrogen and 8 hydrogen.

(26) The n.m.r. analysis of the vinyl region of cycloheptatriene is well known and no discussion of the ring proton assignments seems necessary here; Spectrum No. 158, N. S. Bhacca, L. F. Johnson, and J. N. Shoolery, "NMR Spectra Catalog," Varian Associates, Palo Alto, Calif., 1961.

(27) W. H. T. Davison and G. R. Bates, *J. Chem. Soc.*, 2607 (1953).

Experimental

7-Allylcycloheptatriene.—Allyl chloride (9.2 g., 0.0120 mole) in 20 ml. of anhydrous ether was added to a suspension of magnesium turnings (3.1 g., 0.0128 g.-atom) in 40 ml. of anhydrous ether in a 3-neck flask fitted with a reflux condenser, connected to a drying tube and stirrer. Addition of the allyl chloride required 6 hr. Cycloheptatriene 7-methyl ether (12.0 g., 0.0983 mole) was added dropwise to the cooled, stirred Grignard solution, requiring 30 min. The resulting solution was allowed to warm to room temperature and was stirred for an additional 5.5 hr. The reaction mixture was acidified with 100 ml. of 10% HCl. The aqueous layer was separated and extracted with two 50-ml. portions of ligroin (b.p. 30–60°). The organic layers were combined, dried over magnesium sulfate, and distilled through a 30-cm. Vigreux column to remove the solvents. Vapor phase chromatographic analysis of the pale yellow oil on a DEGS column indicated that it contained 4.4 g. (34%) of 7-allylcyclo-heptatriene. Hydrogenation with Adams catalyst indicates 3.92 double bonds. Infrared spectrum neat had bands at (cm.$^{-1}$): CH, 3030 (s), 3000 (s), 2890 (m), 2820 (s); C=C, 1630 (s); CH bending, 1435 (m), 1410 (s), 1399 (m), 991 (s), 913 (s); ultraviolet spectrum in n-heptane 257 mμ (3310).

Anal. Calcd. for C$_{10}$H$_{12}$: C, 90.93; H, 9.07. Found: C, 90.68, 90.61; H, 9.26, 9.19.

Allyltropenium Hexachloroantimonate.—7-Allylcycloheptatriene (0.334 g., 2.53 mmoles) dissolved in 10 ml. of distilled methylene chloride was added to a solution of triphenylcarbonium hexachloroantimonate (1.67 g., 2.85 mmoles) in 15 ml. of distilled methylene chloride. The reaction was complete in 3 min. with the formation of a white crystalline precipitate. The crystalline product was filtered, washed repeatedly with distilled methylene chloride, and dried to give 1.82 g. (72%) of allyl-tropenium hexachloroantimonate as grayish white needles which decomposed at 84–85°; ultraviolet spectrum in acetonitrile 360 (2640) and 266 mμ (13750); infrared spectrum KBr (cm.$^{-1}$): CH, 3018 (w), 3030 (w); C=C, 1600 (w), 1640 (w); CH bending, 1485 (s), 1450 (s), 998 (s), 942 (s).

The n.m.r. spectrum of this salt in acetonitrile solvent exhibited peaks at 0.88 (6, the 7-membered ring protons), 3.8 (1, multiplet, the inner vinyl proton), 4.5 and 4.72 (2, the AB part of an ABX system; the terminal vinyl protons), and 5.83 τ (2, doublet; the methylene protons), which is consistent with the assigned structure.

Anal. Calcd. for C$_{10}$H$_{11}$SbCl$_6$: C, 25.79; H, 2.38. Found: C, 26.35, 26.22; H, 2.45, 2.53.

Triphenylmethane was recovered from the filtrate by evaporating to dryness, dissolving the residue in benzene, extracting several times with concentrated sulfuric acid, and finally by chromatography over alumina to give white needles, 0.617 g. (85.2%), m.p. 90.5–91.5° (lit. m.p. 92.5°).

Allyltropenium Fluoroborate.—7-Allylcycloheptatriene (0.475 g., 3.59 mmoles) dissolved in 10 ml. of distilled chloroform was added to a solution of triphenylcarbonium fluoroborate (1.20 g., 3.64 mmoles) in 15 ml. of distilled chloroform. The reaction proceeded slowly, partially due to the fact that triphenylcarbonium fluoroborate is only partially soluble in the solvent. The reaction was complete in 30 min. with the formation of a dark green oil which floated on the surface of the reaction mixture. The solvent was removed with a dropper and the residual oil washed with two 10-ml. portions of chloroform. The oil which remained after removal of the chloroform could not be induced to crystallize. The n.m.r. spectrum of a 50–50 mixture of the oil and chloroform exhibited a sharp peak at 0.97 (6, the ring protons), a multiplet at 4.1 (1, the inner vinyl proton), a multiplet at 4.8 (2, the terminal vinyl protons), and a doublet at 6.05 τ (2, the methylene protons). This n.m.r. was completely consistent with allyltropenium fluoroborate.

Triphenylmethane was recovered from the chloroform by extraction with two 50-ml. portions of concentrated sulfuric acid and evaporation of the chloroform to give the crude product. Recrystallization from ethanol–water gave 0.690 g. (78.6%) of triphenylmethane, m.p. 91.5–92°.

8-Vinylheptafulvene.—Allylcycloheptatriene (0.361 g., 2.84 mmoles) which had been freshly purified by vapor phase chromatography, in 5 ml. of distilled chloroform, was added rapidly to a solution of triphenylcarbonium fluoroborate (1.518 g., 3.03 mmoles) in 15 ml. of distilled chloroform. The addition was followed by the slow formation of a greenish oil. The reaction was assumed to be complete after standing at room tem-

perature for 30 min. The oil, after separation from the solvent, was washed with two 3-ml. portions of distilled chloroform. The residual oil was dissolved in 15 ml. of methylene chloride and added rapidly, under nitrogen, to a stirred solution of trimethylamine (5.0 g., 0.0847 mole) in 35 ml. of dichloromethane. The white precipitate of trimethylammonium fluoroborate was removed by filtration and washed with 10 ml. of dichloromethane to give white prisms, 0.216 g. (52%). The filtrate was concentrated to *ca.* 5 ml. with deoxidized nitrogen, then diluted to 20 ml. with carbon tetrachloride and concentrated again. The remaining solution was chromatographed over alumina, under nitrogen, with carbon tetrachloride to yield an intense red solution. The yield could not be determined because of the inability to isolate the final product; infrared spectrum in carbon tetrachloride (cm.$^{-1}$): CH, 3060 (s); C=C, 1606 (m), 1595 (m); CH bending, 1580 (s), 983 (m), 894 (s); ultraviolet spectrum in diethyl ether or cyclohexane 326 (47,900) and 443 mμ (500). The infrared spectrum of the trimethylammonium fluoroborate was identical with that of an authentic sample.

Hydrogenation of 8-Vinylheptafulvene.—To determine the extinction coefficient of the ultraviolet spectrum, 8-vinylheptafulvene was dissolved in diethyl ether which was used as the solvent instead of carbon tetrachloride in the preceding preparation. An aliquot was removed and diluted to determine the ultraviolet spectrum and the remaining solution was hydrogenated using Adams catalyst. The concentration of the propylcycloheptane obtained was determined by vapor phase chromatographic analysis on a DEGS column. The chromatogram consisted of only two peaks which were the solvent and propylcycloheptane. The infrared spectrum of the n-propylcycloheptane obtained was superimposable upon that of n-propylcycloheptane derived from cycloheptanone and n-propylmagnesium bromide.

n-Propylcycloheptatriene.—n-Propyl bromide (7.0 g., 0.057 mole) was added to magnesium turnings (5.1 g., 0.21 mole) in 40 ml. of anhydrous ether over a period of 60 min. This Grignard reagent was then cooled in ice while cycloheptatriene 7-methyl ether (5.0 g., 0.041 mole) in diethyl ether (8 ml.) was added dropwise with stirring over a 1-hr. period. Within a few minutes after the beginning of the addition a light gray resinous material started to precipitate. The reaction mixture was stirred at room temperature for 16 hr. and then acidified with a solution of 10 ml. of concentrated HCl in 30 ml. of water. The aqueous layer was separated and extracted with 30 ml. of ligroin (b.p. 30–60°). The ether and ligroin solutions were combined, dried over magnesium sulfate, then concentrated on a rotary evaporator to yield 15.9 g. of a yellow oil. Vapor phase chromatographic analysis on a DEGS column of this oil indicated that it contained 4.42 g. (80.5%) of n-propylcycloheptatriene; infrared neat (cm.$^{-1}$): CH, 2975 (s), 2870 (s), 2830 (s); C=C, 1675 (w), 1590 (w); CH bending, 1453 (s), 1390 (m), 1370 (m).

Anal. Calcd. for C$_{10}$H$_{14}$: C, 89.49; H, 10.51. Found: C, 89.69, 89.73; H, 10.44, 10.44.

Hydrogenation using Adams catalyst gave n-propylcyclo-heptane, the infrared spectrum of which was identical with that of n-propylcycloheptane produced from dehydration of 1-propylcycloheptanol and hydrogenation.

n-Propylcycloheptane.—n-Propyl bromide (9.9 g., 0.0849 mole) was added to a suspension of magnesium turnings (2.21 g., 0.0912 mole) in 25 ml. of anhydrous ether in a 3-neck flask fitted with a reflux condenser connected to a drying tube, and stirrer. Addition of the n-propyl bromide required 30 min. Cycloheptanone (10.0 g., 0.0894 mole) was added dropwise to the cooled, stirred Grignard solution, requiring 45 min. The reaction mixture was stirred at room temperature for 15 min. following the final addition of the ketone, then diluted with 50 ml. of anhydrous ether and acidified with a 20% aqueous solution of ammonium chloride. The aqueous layer was separated and extracted with two 40-ml. portions of ether. The ether solutions were combined, dried over magnesium sulfate, and concentrated to yield 11.8 g. of a light yellow oil. Vapor phase chromatographic analysis on a DEGS column indicated that the oil contained 4.57 g. (35%) of 1-propylcycloheptanol.

Anal. Calcd. for C$_{10}$H$_{20}$O: C, 76.86; H, 12.90. Found: C, 76.76, 76.89; H, 12.54, 12.60.

Potassium bisulfate (0.5 g., 3.68 mmoles) was added to 3.0 g. of the crude alcohol in 5.0 ml. of cyclohexane and refluxed for 10 hr. The reaction mixture was then distilled and the residue was hydrogenated using platinum oxide. Vapor phase chromatographic analysis of the resulting solution showed that it contained some unreacted alcohol, as well as n-propylcycloheptane.

[Contribution from the Department of Chemistry, The Pennsylvania State University, University Park, Pa.]

Stereochemical Evidence for Bridged Radicals. Photobromination of cis- and trans-4-Bromo-t-butylcyclohexane

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Photobromination of cis-4-bromo-t-butylcyclohexane (I) is a highly selective reaction, yielding trans-3-cis-4-dibromo-t-butylcyclohexane (II). By contrast, trans-4-bromo-t-butylcyclohexane is considerably less reactive and less selective to attack by bromine atoms. These results are interpreted in terms of bromine assistance in the transition state and a bridged radical intermediate which opens in accord with the "diaxial rule." This neighboring group effect is operative only with a neighboring axial bromine.

We previously demonstrated that bridged bromine radicals play an important role in photobrominations of alkyl bromides.[1] This paper is concerned with the steric requirements for bromine bridging in a cyclohexane system fixed by the presence of a t-butyl group.

Thaler has reported[2] that the hydrogen abstraction process occurring in the radical–chain photobromination of bromocyclohexane was highly selective, resulting in almost exclusive formation (94%) of trans-1,2-dibromocyclohexane. This result, when contrasted with the less selective bromination of chlorocyclohexane,[2] strongly suggested bromine atom assistance in the hydrogen abstraction step.

Results

Photobromination of cis-4-Bromo-t-butylcyclohexane (I).—Photobromination of cis-4-bromo-t-butylcyclohexane (I) yielded trans-3-cis-4-dibromo-t-butylcyclohexane (II) as the predominant product (>90%). The
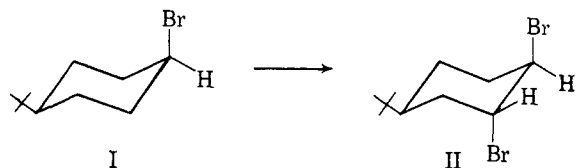
bromination reaction proceeded quickly and gave crude product mixtures, the infrared spectra of which were composites of the spectra of the starting material and the diaxial dibromide II. Vapor phase chromatography (v.p.c.) revealed two peaks in the dibromide region with relative areas of 86:14. A third peak with an area approximately 1% that of the larger peak was also detected. The major peak resulted from the diaxial isomer II while the secondary peak was attributable to cis-3-trans-4-dibromo-t-butylcyclohexane (III). Peak assignments were made by comparing the v.p.c. trace of the crude product with that of a sample containing both isomers II and III. The diaxial dibromide II was prepared by the addition of bromine to 4-t-butylcyclohexene, while the mixture of isomers II and III was obtained by heating a sample of II in a sealed ampoule at 135° for 6 hr.[3] Since the infrared spectrum of the crude product contained no

positive evidence for the dibromide III (characteristic absorptions, particularly at 14.24 and 14.7 μ, were not observed), it was assumed that this isomer resulted in great part from thermal isomerization[3] of the diaxial isomer II in the heated injection block of the gas
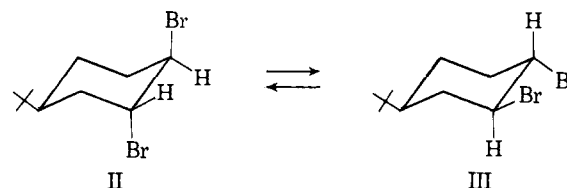
chromatography apparatus. This was supported by the observation that the ratio III:II in a sample as determined by v.p.c. analysis increased as the injection temperature increased. Several small peaks (5%) were also observed with retention times similar to that of the monobromide. One of these was possibly 1-bromo-4-t-butylcyclohexene since it appeared before the peak of the saturated monobromide. Heating a sample of the crude product for 25 hr. at 100° in 80% ethanol[4] did not produce 4-t-butylcyclohexanone in amounts sufficient for detection by gas chromatographic methods, indicating less than 3% 4,4-dibromo-t-butylcyclohexane in the sample.

Additional evidence which supports the above conclusions comes from examination of the n.m.r. spectrum of the crude product (70% dibromide) which showed a characteristic narrow equatorial proton absorption at 283 c.p.s. (base 272–300 c.p.s.) attributable to II and unreacted I. There was only a small nondiscernible broad absorption in the region 220–250 c.p.s. which might be attributed to axial H–C–Br protons, in area less than 6% of the total absorptions in the 220–300 c.p.s. region. Since the starting material contained 3% trans-4-bromo-t-butylcyclohexane (v.p.c.), very little, if any, axial H–C–Br is derived from I.[5]

Photobromination of trans-4-Bromo-t-butylcyclohexane (IV) and cis-3-Bromo-t-butylcyclohexane (V).—An equimolar mixture of trans-4-bromo-t-butylcyclohexane

(1) P. S. Skell, D. L. Tuleen, and P. D. Readio, J. Am. Chem. Soc., **85**, 2849 (1963).

(2) W. Thaler, ibid., **85**, 2607 (1963).

(3) E. L. Eliel and R. G. Haber, J. Org. Chem., **24**, 143 (1959).

(4) The first-order rate constant for solvolysis of 1,1-dibromocyclohexane in 80% ethanol is 75.9 × 10⁻⁸ sec.⁻¹ at 99.8°: H. L. Goering and H. H. Espy, J. Am. Chem. Soc., **78**, 1454 (1956).

(5) Equatorial proton absorptions occur at lower fields, in narrow, relatively unsplit peaks, than similarly substituted axial protons: L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, New York, N. Y., 1959, p. 115; N. O. Brace, J. Am. Chem. Soc., **84**, 3020 (1962).