the entire spectrum, such as the great variation in intensity of *m/e* 71, which could not possibly be laid to this source.

3-Phenyl-2H-thiapyran 1,1-Dioxide (9).—The preparation of this compound has recently been reported.[34] Mercapotacetone, prepared from chloroacetone, was treated with phenacyl bromide in the presence of triethylamine. The diketo sulfide was oxidized to the corresponding sulfone with acidic potassium permanganate, and the sulfone underwent internal aldol condensation in the presence of acetic acid–sodium acetate.

The cyclic keto sulfone was reduced to an alcohol with sodium borohydride, and the alcohol dehydrated with 85% phosphoric acid to yield the desired product. The latter material was taken up in a small volume of methanol, and approximately twice the volume of water was added. After standing overnight in the refrigerator the mixture deposited clear needles, mp 99–101.5° (lit.[34] mp 99–100°). The mass spectrum of this compound was obtained with an ion source temperature of approximately 100° and a slightly warmer probe.

Registry No.—**1,** 4988-33-4; **2,** 17396-35-9; **3,** 17396-36-0; **4,** 1072-72-6; **5,** 17396-38-2; **9,** 6581-28-8.

Acknowledgments.—This study was made possible through the generosity and goodwill of Dr. Gerald Dudek (Harvard Univesity, MS9), Mr. David Quarton (Worcester Foundation for Experimental Biology, M-66), and Dr. Thomas Shannon (Dow Research Laboratory, Wayland, MS12), who obtained the mass spectra. We are also grateful to Dr. E. Molenaar and Professor J. Strating (Groningen) and to Dr. W. L. Mock (Carnegie-Mellon) for information made available prior to publication.

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[34] S. Rossi and G. Pagani, *Tetrahedron Lett.*, 2129 (1966).

Addition of Bromotrichloromethane and Carbon Tetrachloride to Dibenzobicyclo[2.2.2]octatriene

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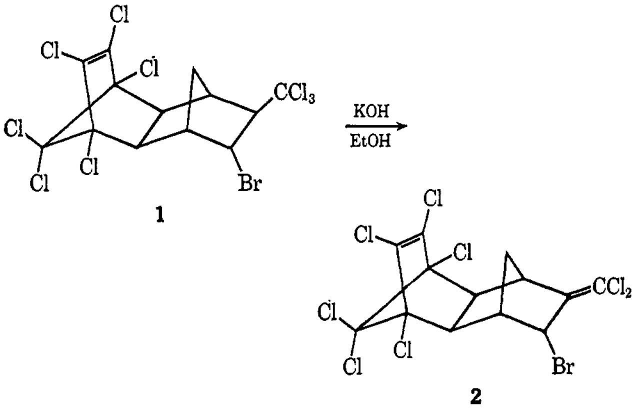
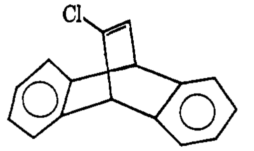
Bromotrichloromethane reacts with dibenzobicyclo[2.2.2]octatriene (**5**) at 105° to give a 1:1 adduct in high yield, whereas the reaction between carbon tetrachloride and **5** at 125–130° (sealed tube) gives a 1:1 adduct in low yield (*ca.* 5%). Both additions occur stereospecifically *trans* and are not accompanied by rearrangement. Upon treatment with base, the 1:1 adduct of bromotrichloromethane and **5** loses both hydrogen chloride (75%) and hydrogen bromide (25%). The 1:1 adduct of **5** and carbon tetrachloride upon treatment with base gives only the exocyclic olefin **8**. Some free-radical and solvolytic reactions of these olefins are discussed.

Additions of carbon tetrahalides to bridged cyclic compounds have been investigated by a number of workers.[1] Bromotrichloromethane reacts readily under free-radical conditions to give 1:1 adducts with norborene,[2,3] bicyclo[2.2.2]octene,[2] norbornadiene,[4,5] aldrin,[6] and hexachloronorbornadiene.[7] The reaction of these compounds with carbon tetrachloride was significantly slower, and in one case[7] the addition reaction failed to take place. Strong evidence has been presented to indicate that these additions to norbornene[3] and aldrin[6] were the result of stereospecific *trans* additions.

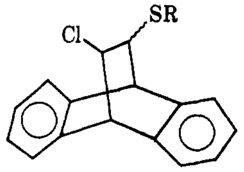
The resulting adducts of bromotrichloromethane with norbornene and bicyclo[2.2.2]octene were inert to 0.7 *N* potassium hydroxide in ethanol at 50° for 6 hr.[2] However, later it was shown that the 1:1 adducts of both carbon tetrachloride and bromotrichloromethane with norbornene lost hydrogen chloride in alcoholic potassium hydroxide to give 2-dichloromethylene-*endo*-3-chloro(bromo)norbornane. Also, the 1:1 adduct (**1**) of bromotrichloromethane and aldrin underwent dehydrohalogenation under similar conditions to give as the only observable product the exocyclic olefin **2**, the result of dehydrochlorination.[6]



In the free-radical addition of thiols to 7-chlorodibenzobicyclo[2.2.2]octatriene (**3**) the stereochemistry of the products depended on the mercaptans used. Both *p*-thiocresol[8] and methyl mercaptan[9] gave mixtures of *cis* and *trans* adducts **4**.



3



4

Results and Discussion

The addition of bromotrichloromethane to dibenzobicyclo[2.2.2]octatriene (**5**) went smoothly in neat

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[1] For reviews in this area, see (a) D. I. Davies and S. J. Cristol in "Advances in Free-Radical Chemistry," Vol. 1, G. H. Williams, Ed., Logas Press, London, 1965, p 155; (b) G. Sosnovsky, "Free Radical Reactions in Preparative Organic Chemistry," The Macmillan Co., New York, N. Y., 1964, Chapter 2.

[2] M. S. Kharasch and H. N. Friedlander, *J. Org. Chem.*, **14**, 239 (1949).

[3] E. Tobler and D. J. Foster, *ibid.*, **29**, 2839 (1964).

[4] D. J. Trecker and J. P. Henry, *J. Amer. Chem. Soc.*, **85**, 3204 (1963).

[5] D. I. Davies, *J. Chem. Soc., C*, 2691 (1967).

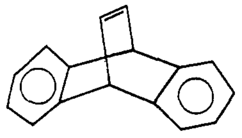
[6] D. I. Davies, *ibid.*, 3669 (1960).

[7] J. A. Clasisse, D. I. Davies, and C. K. Alden, *ibid.*, 1498 (1966).

[8] S. J. Cristol and R. P. Arganbright, *J. Amer. Chem. Soc.*, **79**, 6039 (1957).

[9] S. J. Cristol, R. Caple, R. M. Sequeira, and L. O. Smith, Jr., *ibid.*, **87**, 5679 (1965).

bromotrichloromethane at the boiling point (105°) with a catalytic amount of benzoyl peroxide present. The adduct (**6**) obtained in essentially quantitative yield was shown by nmr analysis to be the *trans* adduct. An nmr spectrum of the reaction mixture showed only **6** present with none of the corresponding *cis* isomer observable. The reaction of **5** with carbon tetrachloride at elevated temperature (125–130°) in the presence of benzoyl peroxide gave the *trans* compound **7** as the only observable 1:1 adduct, albeit in low yield.



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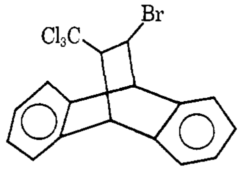
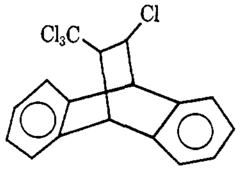
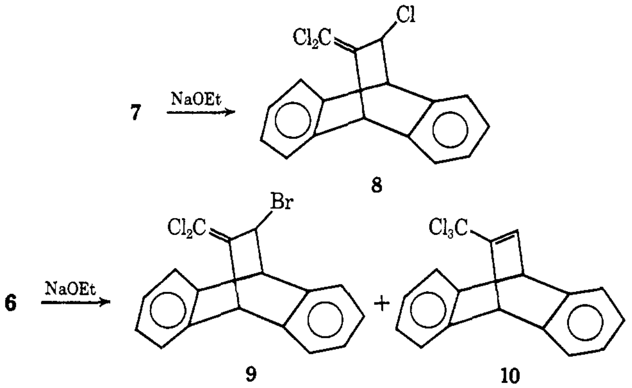


6



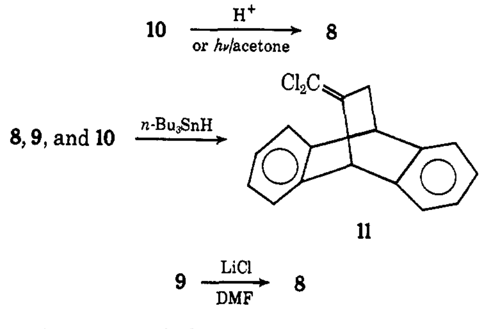
7

Treatment of **7** with sodium ethoxide in ethanol gave the exocyclic olefin **8** while under similar conditions **6** gave a 3:1 mixture of the exocyclic olefin **9** and the endocyclic olefin **10**, respectively. The olefins **9** and **10** were separated by fractional crystallization from hexane.

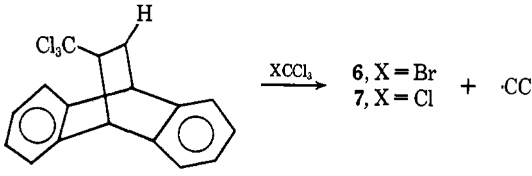


The endocyclic olefin **10** underwent isomerization to the exocyclic olefin **8** under mild conditions [chromatography over silica gel, treatment with anhydrous hydrogen chloride in ether, heating at the melting point (*ca.* 165°), or standing in methanol solvent at room temperature, the latter being accompanied by methanolysis]. Furthermore, an attempt to isomerize **10** to the dibenzotricyclo$[3.3.0.0^{2,8}]$octadiene system by irradiation in acetone solution (Pyrex filter), conditions known[10] to bring about similar rearrangements of dibenzobicyclo[2.2.2]octatrienes, gave the allylic isomer **8**. With direct irradiation in ether or hexane, **10** disappeared but gave unidentifiable material. Under these conditions, **8** was stable toward irradiation.

Both **9** and **10** were treated with 1 equiv of tributyltin hydride at 80° in benzene to give the exocyclic olefin **11**. Under these conditions, the trichloromethyl olefin **10** reacted about twice as fast as the allylic bromide **9**. Since the allylic chloride **8** was far less reactive toward tributyltin hydride than was **9** or **10**, it was necessary to use higher temperatures (132°) in order for the reaction **8** → **11** to take place at an appreciable rate. The relationship between the allylic halides **8** and **9** was illustrated by the conversion of **9** into **8** with lithium chloride in N,N-dimethylformamide (DMF).



The assignment of the *trans* configurations to **6** and **7** rests on the observed coupling constants (J values) between the C-7 and C-8 protons. For **6**, J_{78} = 4.4 Hz, and for **7** J_{78} = 4.2 Hz, which agree well with the $J_{7,8}$ values reported[11] for analogous *trans*-substituted dibenzobicyclo[2.2.2]octadienes but are not within the range ($J_{cis\text{-}78}$ = 8.8 ± 0.8 Hz) reported[11] for the corresponding *cis* compounds. The assignment of the chemical shifts (see Experimental Section) to the aliphatic protons in **6** and **7** is based on the observed coupling constants and the observation that the chemical shift of the proton α to the trichloromethyl group occurs *ca.* 1 ppm upfield[3] from the proton α to the halogen atom; the position of the latter is based on assignments made on closely related compounds.[11] As in the case of previous free-radical additions to dibenzobicyclo[2.2.2]octatrienes,[8,9] no products of Wagner–Meerwein rearrangement were observed, although such rearrangements were observed in bicyclo[2.2.1]heptadiene systems.[7,12,13] The stereochemistry of these additions to **5** can be attributed to the steric requirement of the bulky trichloromethyl group which, in the chain-transfer step to the intermediate radical **12**,[3] hinders the approach of the carbon tetrahalide molecule from the *cis* side.



12

The base-catalyzed elimination of hydrogen halide from **6** gave a 3:1 mixture of **9** (loss of hydrogen chloride) and **10** (loss of hydrogen bromide), respectively, while, under these same conditions, **7** gave only the exocyclic olefin **8**. The assignment of the structures of **8**, **9**, and **10** follows from their mode of synthesis and the patterns of the nmr spectra. In deuteriochloroform **8** gives three absorptions (1 H each) outside the aromatic region: a singlet at τ 4.68 and a pair of doublets at 5.20 and 5.42 (J_{48} = 3.5 Hz). For **9**, the

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(10) E. Ciganek, *J. Amer. Chem. Soc.*, **88**, 2882 (1966).

(11) S. J. Cristol, T. W. Russell, J. R. Morig, and D. E. Plorde, *J. Org. Chem.*, **31**, 581 (1966).

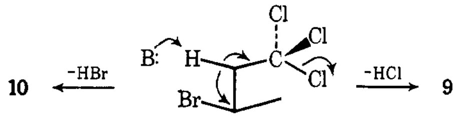
(12) C. K. Alden, J. A. Claisse, and D. I. Davies, *J. Chem. Soc.*, 1540 (1966).

(13) S. J. Cristol and G. W. Nachtigall, *J. Org. Chem.*, **32**, 3727 (1967).

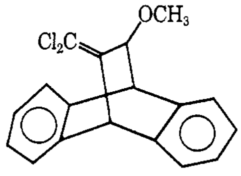
corresponding protons appear at τ 4.73 (singlet), 5.18, and 5.42 (J_{48} = 3.4 Hz). In carbon tetrachloride solvent, the chemical shift for the C-4 and C-8 protons in the allylic chloride **8** appears *ca.* 6–10 Hz upfield from the allylic bromide **9**. This small upfield shift in going from bromides to chlorides is typical of secondary halides.[14] The nmr spectrum of **10** shows a complex pattern of protons from τ 2.5 to 3.2 (9 H) and two doublets (1 H each) located at 4.53 (J_{18} = 2.2 Hz) and 4.85 (J_{48} = 6.4 Hz). The allylic coupling J_{18} is not observable in 7-chlorodibenzobicyclo[2.2.2]octatriene (**3**), but the vicinal coupling (J_{48} = 6.0 Hz) in **3** is on the same order as that observed in **10**.[11] Also, the carbon–carbon double-bond stretching ($\nu_{C=C}$) in **8** and **9** is very strong, typical of the dichloromethylene group,[15] whereas $\nu_{C=C}$ for **10** is relatively weak.

Because of the rigidity of the system in **6**, the loss of hydrogen bromide must be *cis* and coplanar while loss of hydrogen chloride presumably will occur in a *trans* coplanar (antiperiplanar) manner in the E2 elimination[16] (Scheme I). The inherent propensity for loss of hydrogen bromide over loss of hydrogen chloride (*ca.* a factor of 50 in favor of loss of hydrogen bromide[17]) appears to compete with the *trans* elimination of hydrogen chloride.[18–20] However, several factors tend to complicate simple interpretation of the data. First, it is clear from earlier work[21] that the relative reactivity of chlorine as a leaving group from trichloromethyl compounds is not expected to have the same relative reactivity as the typical alkyl chloride. From the product distribution observed in the base-catalyzed loss of hydrogen chloride from 1,1,1,3-tetrachloropropane (about a 2:1 mixture of 3,3,3-trichloropropene and 1,1,3-trichloropropene, respectively),[22] it appears that the ability of chlorine to act as a leaving group in E2 eliminations diminishes when it becomes the member of a trichloromethyl group. Treatment of the 1:1 adducts of bromotrichloromethane and typical acyclic olefins with base most often gives rise only to loss of hydrogen bromide.[1b,22] However, analogous adducts of bicyclic olefins react with base to give only the exocyclic olefins, the result of loss of hydrogen chloride.[1,3–7] Another difficulty in interpreting the product distribution in the reaction of **6** with base is the obvious difference in the stabilities of the resulting olefins **9** and **10** (*vide infra*). The higher the double-bond character in the transition state of these E2 reactions, the correspondingly more favorable will be the formation of the more stable olefin (**9**).

SCHEME I



Attempts to separate **9** and **10** by chromatography over silica gel led to the isomerization of **10** to its allylic isomer **8**. Subsequently, it was shown that **10** isomerizes to **8** under mild conditions (*vide supra*). Compounds resembling **10**, in that they possess a trichloromethyl group bound to a carbon–carbon double bond, are known to undergo analogous rearrangements under acidic[15,23–25] and free-radical conditions.[26] It is clear from thermodynamic studies on 3,3,3-trichloropropenes[26] that the allylic isomers, 1,1,3-trichloropropenes, are far more stable. The high reactivity of **10** toward solvolysis is illustrated by its behavior in absolute methanol. After standing at room temperature for 15 hr, **10** gave 30% recovered starting material, 14% allylic isomer **8**, and 56% methyl ether **13**. The presence of 0.15 M potassium hydroxide had no appreciable effect on either the rate or product distribution of this reaction, clearly indicting that in methanol **10** solvolyzes by a unimolecular process (SN1). Under these same conditions, neither the allylic chloride **8** nor the allylic bromide **9** showed any signs of solvolyzing.[27] When treated with silver perchlorate in methanol, **8**, **9**, and **10** all gave the methyl ether **13**.



13

In the methanolysis of **10**, the only observed products are the rearranged chloride **8** (which slowly gives **13**) and the methyl ether **13**. The fact that no unrearranged methyl ether **14** was detected should be noted in view of the previous observations that under kinetic conditions the more unstable allylic isomer often is found to predominate in SN1 solvolysis of allylic halides.[28] However, solvolysis of 3-bromo-2-methylenenorborane[29] under SN1 conditions gives a 2:1 mixture

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(14) L. M. Jackman, "Nuclear Magnetic Resonance Spectroscopy," Pergamon Press, New York, N. Y., 1959, p 54.

(15) J. R. Shelton and L. Lee, *J. Org. Chem.*, **23**, 1876 (1958).

(16) D. Banthrope, "Elimination Reactions," Elsevier Publishing Co., New York, N. Y., 1963.

(17) R. A. Bartsch and J. F. Bunnett, *J. Amer. Chem. Soc.*, **90**, 408 (1968).

(18) The implication that the *trans* elimination of HX should be more favored than *cis* elimination of HX in this system may not be true. It was pointed out recently[19,20] that the difference in rate between *cis* and *trans* eliminations may be due primarily to steric effects (*e.g.*, eclipsing effects) rather than to stereoelectronic control. However, since the base presumably approaches **6** in the same manner for *cis* and *trans* elimination, the steric factors are essentially the same no matter which pathway is taken (Scheme I). Unfortunately, nothing can be said about the relative ease of *cis vs. trans* eliminations in this system since the products depend on the mode of elimination adapted.

(19) C. H. Depuy, G. F. Morris, J. S. Smith, and R. J. Smat, *ibid.*, **87**, 2421 (1965).

(20) D. J. McLennan, *Quart. Rev.* (London), **21**, 490 (1967). See, however, E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," John Wiley & Sons, Inc., New York N. Y., 1965, pp 483, 484.

(21) S. J. Cristol, N. L. Hause, A. J. Quant, H. W. Miller, K. R. Eilar, and J. S. Meek, *J. Amer. Chem. Soc.*, **74**, 3333 (1952).

(22) W. Reeve and L. W. Fine, *Can. J. Chem.*, **41**, 2231 (1963).

(23) D. G. Kundiger and H. N. Haney, *J. Amer. Chem. Soc.*, **76**, 615 (1954).

(24) C. H. Shuford, Jr., D. L. West, and H. W. Davies, *ibid.*, **76**, 5803 (1954).

(25) F. Boberg, H. Khalaf, and K. Kirchhoff, *Tetrahedron Lett.*, 5181 (1967).

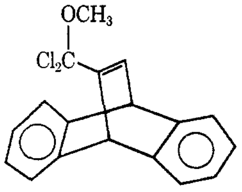
(26) A. N. Nesmeyanov, R. Kh. Freidlina, and V. I. Firstov, *Dokl. Akad. Nauk SSSR*, **78**, 717 (1951).

(27) The kinetics of these and related reactions will be reported at a later date. Preliminary data indicate that the high reactivity of **10** toward SN1 solvolyss compared with that of **8** can be ascribed to the relatively high ground-state energy of **10**. The literature gives little information on the relative reactivities of analogous compounds toward SN1 solvolysis. However, under SN2 (or SN2′) reaction conditions, 1,1,3-trichloropropene appears to be *ca.* six times more reactive than 3,3,3-trichloropropene.[22]

(28) R. H. DeWolfe and W. G. Young in "Chemistry of Alkenes" S. Patai, Ed., Interscience Publishers, New York, N. Y., 1964, p 705.

(29) C. W. Jefford and W. Wajnarowski, *Chem. Commun.*, 129 (1968).

of more stable[30] unrearranged **15** and the less stable endocyclic olefin **16**, respectively. If **14** had formed initially in the reaction of **10** with methanol, it seems likely that **14** might have reacted under the conditions of the reaction to give methyl ketals (acetals) or a methyl ortho ester (or derivatives of these species), but none of these was observed.



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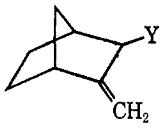
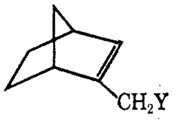


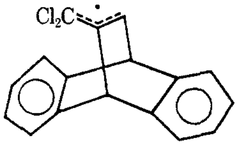
15, Y = OAc, OH



16, Y = OAc, OH

From the data it is obvious that the equilibrium between **8** and **10** lies far toward the side of **8**. Thermodynamic data from the 2-methylbicyclo[2.2.2]octene–2-methylenebicyclo[2.2.2]octane system show the preference for the double bond to be endocyclic in that system.[30] However, the bicyclo[2.2.2]octene system may not be a good model for the dibenzobicyclo[2.2.2]-octatriene system as indicated by the observation that acid-catalyzed dehydration of 7-hydroxy-7-methyldibenzobicyclo[2.2.2]octadiene gave as the only observable product 7-methylenedibenzobicyclo[2.2.2]octadiene.[31] Substitution by the chlorine atom also no doubt affects the position of equilibrium in favor of **8**.[26,32]

The reactions of **8**, **9**, and **10** with tributyltin hydride presumably all lead to the same intermediate allylic radical **17**.[33] The product-determining step occurs in the hydrogen-atom transfer from the tributyltin hydride to **17** which takes place exclusively at one end (C-8) of the allyl system so as to give the more stable product.[34]



17

Experimental Section[35]

8-Bromo-7-trichloromethyldibenzobicyclo[2.2.2]octadiene (6).—A mixture of 3.0 g (14.7 mmol) of dibenzobicyclo[2.2.2]-octatriene (**5**),[8] 8 ml of freshly distilled bromotrichloromethane, and 60 mg of benzoyl peroxide were held at reflux (105°) under 1 atm of nitrogen for 2 hr. An nmr spectrum of the crude reaction mixture showed only **6** present. The excess bromotrichloromethane was removed by rotary evaporation, and the resulting light yellow oil was crystallized from methanol to give 5.5 g (92%) of **6**, mp 134–135°.

The nmr spectrum in carbon tetrachloride shows two doublets (1 H each) at τ 5.27 (J_{17} = 2.0 Hz) and 5.58 (J_{48} = 2.8 Hz), two doublet of doublets (1 H each) at 5.73 (J_{48} = 2.8 Hz, J_{78} = 4.4 Hz) and 6.72 (J_{17} = 2.0 Hz, J_{78} = 4.4 Hz), and a complex multiplet (8 H) for the aromatic protons from 2.6 to 3.1.

Anal. Calcd for $C_{17}H_{12}BrCl_3$: C, 50.72; H, 3.01. Found: C, 50.97; H, 3.04.

8-Chloro-7-trichloromethyldibenzobicyclo[2.2.2]octadiene (7).—A mixture of 3.0 g (14.7 mmol) of **5** and 100 mg of benzoyl peroxide dissolved in 25 ml of carbon tetrachloride was sealed in a Carius tube under nitrogen and heated at 125–130° for 15 hr. The tube was allowed to cool to room temperature and opened; the excess carbon tetrachloride was removed by rotary evaporation. The resulting yellow oil was chromatographed over 150 g of silica gel packed in Skellysolve B. Elution with Shellysolve B gave 1.5 g of an unidentifiable oil whose nmr spectrum (carbon tetrachloride) showed broad absorptions in the aromatic region and in the higher field region of τ 8–9. Elution with 5% benzene in Skellysolve B gave 260 mg (5%) of **7**, recrystallized from ethanol, mp 118–119°.

The nmr spectrum in carbon tetrachloride shows a doublet (1 H) at τ 5.21 (J_{17} = 2.0 Hz) and a doublet of doublets at 6.81 (J_{17} = 2.0 Hz, J_{78} = 4.2 Hz). The doublet (1 H) at 5.60 (J_{48} = 2.9 Hz) and doublet of doublets (1 H) at 5.68 (J_{48} = 2.9 Hz, J_{78} = 4.2 Hz) were overlapping. The aromatic protons (8 H) appeared as a complex multiplet from 2.5 to 3.0.

Anal. Calcd for $C_{17}H_{12}Cl_4$: C, 57.02; H, 3.38. Found: C, 56.93; H, 3.37.

8-Chloro-7-dichloromethylenedibenzobicyclo[2.2.2]octadiene (8).—To a solution of 200 mg (0.56 mmol) of **7** dissolved in 5 ml of ethanol was added 5 ml of 1.3 *M* sodium ethoxide solution. This mixture was held at reflux for 10 min and worked up by pouring it into water and extracting the resulting mixture well with ether. The ether was dried over anhydrous magnesium sulfate and was removed by rotary evaporation. An nmr spectrum of the resulting oil showed only the presence of **8**. The oil was crystallized from methanol to give 150 mg (84%) of **8** ($\nu_{C=C}$ at 1624 cm^{-1}, strong), mp 137–138°.

The nmr spectrum of **8** in deuteriochloroform shows a singlet (1 H) at τ 4.68, a pair of doublets (1 H each, J = 3.5 Hz) at 5.20 and 5.42, and a complex multiplet for the aromatic protons (8 H) from 2.5 to 3.0.

Anal. Calcd for $C_{17}H_{11}Cl_3$: C, 63.48; H, 3.45. Found: C, 63.67; H, 3.47.

Dehydrohalogenation of 6.—To a solution of 8.0 g (19.8 mmol) of **6** dissolved in 10 ml of dioxane was added 40 ml of ethanol in which 0.6 g of sodium metal had been dissolved. The resulting solution was heated at reflux for 1 min, cooled, and poured into water. Work-up with ether gave an oil whose nmr spectrum showed a mixture of 8-bromo-7-dichloromethylenedibenzobicyclo-[2.2.2]octadiene (**9**) (75%) and 7-trichloromethyldibenzobicyclo-[2.2.2]octatriene (**10**) (25%). The oil was dissolved in 30 ml of hexane, and after 2 days 3.3 g of **9** was collected by filtration. The mother liquor yielded 0.90 g of **10**, and successive fractional crystallizations of the mother liquor gave a total of 4.0 g (55%) of **9** ($\nu_{C=C}$ at 1613 and 1622 cm^{-1}, strong), mp 126–127°, and 1.25 g (20%) of **10** ($\nu_{C=C}$ at 1630 cm^{-1}, weak), mp 165–167°.[36]

The nmr spectrum of **9** in deuteriochloroform shows a singlet (1 H) at τ 4.73, two doublets (1 H each, J = 3.4 Hz) at 5.18 and 5.42, and a complex multiplet for the aromatic protons (8 H) from 2.6 to 3.1.

Anal. Calcd for $C_{17}H_{11}BrCl_2$: C, 55.77; H, 3.03. Found: C, 55.48; H, 3.13.

The nmr spectrum of **10** in deuteriochloroform shows two doublets (1 H each) at τ 4.53 (J = 2.2 Hz) and 4.85 (J = 6.4 Hz) and a complex multiplet (9 H) from 2.5 to 3.2.

Anal. Calcd for $C_{17}H_{11}Cl_3$: C, 63.48; H, 3.45. Found: C, 63.30; H, 3.53.

Irradiation of 10.—A solution of 200 mg of **10** in 20 ml of acetone was irradiated with a 450-W Hanovia type L lamp (Pyrex

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(30) In this system, equilibria data show that 2-methylenenorbornane is considerably more stable than 2-methylnorbornene: calculated from the data given in Table III by S. Bank, C. A. Rowe, Jr., A. Schriesheim, and L. A. Naslund, *J. Amer. Chem. Soc.*, **89**, 6897 (1967); see also G. Van Binst and Y. Merck, *Tetrahedron Lett.*, 3897 (1967).

(31) V. J. Shiner and J. S. Humphrey, Jr., *J. Amer. Chem. Soc.*, **85**, 2416 (1963).

(32) Reference 28, p 723.

(33) H. G. Kuivila, *Advan. Organometal. Chem.*, **1**, 76 (1964).

(34) J. Mantecón, L. Cortés, E. Payo, and C. Piemonti, *J. Org. Chem.*, **33**, 1235 (1968).

(35) Melting points were determined on a Fisher-Johns apparatus and are uncorrected. Nuclear magnetic resonance spectra were measured with a Varian A-60A nmr spectrometer with tetramethylsilane (τ 10.00) as the internal standard. J values reported are "observed" ones. Infrared spectra were measured in carbon tetrachloride solution on a Beckman IR-5 infrared spectrometer. The ultraviolet spectrum of **10** was measured in hexane solution, using a Cary 14 uv spectrometer. Elemental analyses were performed by Dr. Franz J. Kasler, University of Maryland.

(36) If the melting point of **10** is taken slowly, the melting point range is large (*viz.* 148–160°). This is due no doubt to the isomerization of **10** to **8**; when **10** was heated neat at 165–170° for 1 hr, the resulting material had mp 125–127°, undepressed on admixture with **8**. The melting point given for **10** was determined by dropping a crystal of **10** on the melting point block which was heated to a temperature near the melting point.

filter) for 2 days. An nmr spectrum of the resulting orange-brown reaction solution showed a mixture of **8** and **10** in the ratio of *ca.* 95:5, respectively, and a small amount of material whose absorptions in the nmr spectrum were very broad high field (τ 8–9) signals. This same contaminant was observed when **8** was irradiated under these same conditions.

Irradiation of **10** for 2 days in ether or hexane (in the presence or absence of benzophenone) gave no readily identifiable material (again, only broad signals were observed in the nmr spectrum). Under these conditions, **8** showed <10% decomposition.

The uv spectrum of **10** in hexane [λ 256 mμ (ϵ 2400), 267 (2550), 272 (3200), and 278 (3570)] agrees well with those published for similarly substituted dibenzobicyclo[2.2.2]octatrienes.[37,38]

7-Dichloromethylenedibenzobicyclo[2.2.2]octadiene (11).—A mixture of 1.5 g (4.1 mmol) of the allylic bromide **9** and 1.2 g (4.1 mmol) of tributyltin hydride[39] was heated at reflux in 20 ml of dry benzene under nitrogen for 20 hr (an nmr spectrum of the reaction mixture after 3 hr showed that the reaction was about 50% complete). The benzene was removed by rotary evaporation, and the resulting oil was chromatographed over 100 g of silica gel packed in Skellysolve B. Tributyltin bromide was eluted with Skellysolve B, and elution with 5% benzene in Skellysolve B gave 1.0 g (85%) of **11** ($\nu_{C=C}$ at 1625 cm^{-1}, strong), mp 123–124° (from methanol).

The nmr spectrum in carbon tetrachloride shows a singlet (1 H) at τ 4.76, a triplet (1 H, J_{48} = 2.9 Hz) at 5.67, a doublet (1 H) at 7.55, and a complex multiplet (8 H) from 2.6 to 3.1.

Anal. Calcd for $C_{17}H_{12}Cl_2$: C, 71.10; H, 4.21. Found: C, 71.31; H, 4.28.

Under these same conditions, **10** had a half-life of *ca.* 1.5 hr and gave **11** as the only observable (nmr analysis) product (isolated in 85% yield). The allylic chloride **8** under these conditions showed <5% reaction after 10 hr. Use of refluxing chlorobenzene (132°) as the solvent (0.30 g of **8**, 0.29 g of tributyltin hydride, and 10 ml of chlorobenzene under nitrogen) gave complete conversion of **8** into **11** after 1 day.

Reaction of 9 with Lithium Chloride in N,N-Dimethylformamide (DMF).—A solution of 2.0 g (5.5 mmol) of **9** and 5.0 g of anhydrous lithium chloride dissolved in 25 ml of dry DMF was held at 90–95° for 1 day. The mixture was poured into water and extracted well with ether. The ether was dried over anhydrous magnesium sulfate. The ether was removed by rotary evaporation, and the resulting oil was crystallized from ethanol to give 1.7 g (96%) of **8**, mp and mmp 137–138°.

Isomerization of 10 to 8.—An attempt to separate a mixture of **9** and **10** (3:1, respectively) by passing the mixture over silica gel gave a mixture of **9** and **8** (3:1, respectively.). The nmr and ir spectra of this resulting mixture were identical with the ir and nmr spectra of a synthetic mixture of **9** and **8** (3:1, respectively). When pure **10** was eluted through a column of silica gel (20:1, silica gel/**10** by weight) with 5% benzene in Shellysolve B, a quantitative conversion into **8** was realized.

Treatment of 200 mg of **10** in 20 ml of 2% anhydrous hydrogen chloride in ether solution at room temperature for 6 hr gave complete conversion into the allylic isomer **8**.

Methanolysis of 10.—A solution of 100 mg of **10** in 20 ml of methanol stood at room temperature for 15 hr. The methanol was removed at 0° under reduced pressure, and an nmr spectrum of the resulting oil showed a mixture of 30% **10**, 14% allylic isomer **8**, and 56% methyl ether **13**. Under these same conditions in 0.15 *M* potassium hydroxide in methanol, **10** gave 28% **10**, 12% **8**, and 60% **13** (nmr analysis). Under identical conditions, in the presence or absence of base, the allylic halides **8** and **9** gave no reaction.

Heating 200 mg (0.62 mmol) of **10** in methanol at reflux for 1 hr gave *ca.* 4:1 mixture of **13**/**8**, respectively. From this mixture was crystallized 110 mg (56%) of 8-methoxy-7-dichloromethylenedibenzobicyclo[2.2.2]octadiene (**13**) ($\nu_{C=C}$ at 1630 cm^{-1}, strong), mp 137–139°.

A mixture of 200 mg (0.62 mmol) of the allylic chloride **8** and 200 mg of anhydrous silver perchlorate was heated at reflux in 15 ml of methanol for 1 hr. Work-up gave 180 mg (91%) of **13**. Under these same conditions, **9** and **10** gave essentially identical results.

The nmr spectrum of **13** in deuteriochloroform shows two singlets at τ 4.81 (1 H) and 6.67 (3 H), two doublets (1 H each, J = 3.6 Hz) at 5.40 and 5.96, and a complex multiplet for the aromatic protons (8 H) from 2.6 to 3.2.

Anal. Calcd for $C_{18}H_{14}Cl_2O$: C, 68.15; H, 4.45. Found: C, 68.17; H, 4.48.

Registry No.—Bromotrichloromethane, 75-62-7; carbon tetrachloride, 56-23-5; **5**, 2734-13-6; **6**, 17519-19-6; **7**, 17497-39-1; **8**, 17497-43-7; **9**, 17497-40-4; **10**, 17497-41-5; **11**, 17497-42-6; **13**, 17519-20-9.

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