Reaction of Norbornenone with Morpholine (No Acid Catalyst.)—A stirred solution of 10.8 g (0.1 mol) of norbornenone, 8.7 g (0.1 mol) of morpholine, and 150 ml of xylene was refluxed under a nitrogen atmosphere for 114 hr. Water was removed during this time by means of a Dean-Stark trap. At the end of this time the solvent and excess starting materials were removed and the residual oil was fractionally distilled. The product distribution is 0.19 g (1%) of ***exo*-5-*N*-morpholinobicyclo[2.2.1]heptan-2-one (8)** (identified by glc and ir spectral comparison with an authentic sample[5]), 0.54 g (3%) of ***endo*-2-*N*-morpholinobicyclo[2.2.1]hept-5-ene (7)** (identified by glc and ir spectral comparison with an authentic sample, see below), 0.55 g of **2-*N*-morpholinobicyclo[2.2.1]hepta-2,5-diene (6)** (identified by hydrogenation to a known saturated amine, ir spectra, and independent synthesis, see below), and 4.45 g (17%) of **2,5-bis-(*N*-morpholino)tricyclo[2.2.1.0^{2,6}]heptane (5)** (identified by comparison with an authentic sample[5]). See Table I for comparison of yields for different reaction times. The balance of the reactants were recovered as unreacted starting materials.

***exo*-2-*N*-Morpholinobicyclo[2.2.1]heptane (13).**—A solution of 18.4 g (0.094 mol) of *exo*-5-*N*-morpholinobicyclo[2.2.1]heptan-2-one (8),[5] 135 ml of diethylene glycol, 34 g of potassium hydroxide, and 24 ml of 85% hydrazine hydrate was stirred at 60–120° for 6 hr and at 220° for 3 hr. Then ~1.5 l. of steam distillate was obtained and extracted with ether, the combined extracts were dried over anhydrous magnesium sulfate and filtered, and the solvent was removed and distilled. A total of 5.6 g (37%) of colorless product was obtained, bp 80° (0.6 mm), n^{27}D 1.4972.

Anal. Calcd for $C_{11}H_{19}NO$: C, 72.88; H, 10.56. Found: C, 73.03; H, 10.57.

***endo*-2-*N*-Morpholinobicyclo[2.2.1]heptane (9).**—A stirred slurry of 5.1 g (0.018 mol) of the perchlorate salt of 2-*N*-morpholinobicyclo[2.2.1]hept-2-ene (14), 3.8 g (0.1 mol) of lithium aluminum hydride and 500 ml of ether was refluxed for 21 hr. The reaction mixture was treated with an aqueous saturated sodium sulfate solution and filtered, the solvent was removed, and residual oil was distilled. A total of 2.3 g (71%) of colorless liquid product was obtained, bp 76° (0.65 mm), n^{26}D 1.4953.

Anal. Calcd for $C_{11}H_{19}NO$: C, 72.88; H, 10.56. Found: C, 72.95; H, 10.60.

***endo*-5-*N*-Morpholinobicyclo[2.2.1]heptan-2-one (15).**—A solution of 5.34 g (0.03 mol) of 5-*N*-morpholinobicyclo[2.2.1]hept-5-en-2-one (16)[20] and 75 ml of ethyl acetate was hydrogenated using 10% palladium-on-carbon catalyst and 40-psi pressure. After filtration and solvent removal, the residual liquid was distilled to give 3.6 g (66%) of a colorless product, bp 111° (0.35 mm).

Anal. Calcd for $C_{11}H_{17}NO_2$: C, 67.66; H, 8.78. Found: C, 67.37; H, 8.99.

A Wolff–Kishner reduction was run on this product by a procedure identical with that used to reduce amino ketone **8**. *endo*-2-*N*-Morpholinobicyclo[2.2.1]heptane (**9**) was the product obtained in a 30% yield.

3-Methylbicyclo[2.2.1]heptane-2,5-dione (18).—A stirred mixture of 2.43 g (0.013 mol) of 5-*N*-morpholinobicyclo[2.2.1]-hept-5-en-2-one (16)[20] and 226 g of methyl iodide was refluxed for 16 hr. The cooled solution was filtered, the solid residue as refluxed with dilute hydrochloric acid for 1.5 hr and extracted with ether, the combined extracts were dried over anhydrous magnesium sulfate and filtered, and solvent was removed. A total of 0.6 g (33%) of colorless liquid product was obtained, bp 124° (15 mm). It solidified on standing, mp 35–36.5°.

Anal. Calcd for $C_8H_{10}O_2$: C, 69.54; H, 7.30. Found: C, 69.71; H, 7.32.

Reaction of 1,1-Dimorpholinoethene with Cyclopentadiene.—A mixture of 3.3 g (0.05 mol) of freshly distilled cyclopentadiene, 9.9 g (0.05 mol) of 1,1-dimorpholinoethene[11] and a trace of hydroquinone was heated in a reaction bomb at 120–130° for 7 hr. At the end of this time the bomb was cooled, and a total of 0.22 g (3%) of 2-*N*-morpholinobicyclo[2.2.1]hepta-2,5-diene (6) was found. It was identified by ir and glc with an authentic sample.

***endo*-2-*N*-Morpholinobicyclo[2.2.1]hept-5-ene (7).**—A stirred mixture of 6.0 g (0.055 mol) of norbornenone (4), 10.3 g (0.055 mol) of morpholine perchlorate, and 100 ml of xylene was refluxed under nitrogen for 2 hr, and water was removed with a Dean-Stark trap. The solvent was decanted, and 120 ml of ether and 3.8 g (0.1 mol) of lithium aluminum hydride was added. The stirred reaction mixture was refluxed for 17 hr, after which it was treated with a saturated solution of sodium sulfate. The mixture was filtered, the solvent was removed, and the residual oil was distilled. A total of 3.83 g (39%) of product was obtained as a colorless liquid, bp 62° (0.15 mm), n^{23}D 1.5057, nmr δ 5.90 (2 H, m, HC=CH), $\lambda_{\max}^{\text{cyclohexane}}$ 203 nm (ϵ 5700).

Anal. Calcd for $C_{11}H_{17}NO$: C, 73.71; H, 9.56. Found: C, 73.85; H, 9.64.

Registry No.—**7**, 34201-83-7; **9**, 20238-39-5; **13**, 34217-00-0; **15**, 34217-01-1; **16**, 34219-66-4; **18**, 34219-67-5; **22**, 34219-68-6; **24**, 34219-69-7.

---

[20] See Table II for synthetic method and physical properties.

Distal Effects in E2 Eliminations. Elimination of Hydrogen Chloride from Epimeric 8-Trichloromethyldibenzobicyclo[3.2.1]octadienes[1]

BRUCE B. JARVIS* AND JOHN P. GOVONI

Department of Chemistry, University of Maryland, College Park, Maryland 20742

Received August 6, 1971

A series of C-4 substituted epimeric 8-trichloromethyldibenzobicyclo[3.2.1]octadienes were synthesized and their rates of elimination with lithium chloride in dimethylacetamide (DMA) measured. The substituents at C-4 have a marked effect on the rates for loss of hydrogen chloride from the *anti*-8-trichloromethyl epimers but have no apparent effect on the rates for the syn epimers. The $k_{\text{syn}}/k_{\text{anti}}$ ranged from 48 to 2300 depending upon the substituent at C-4. This large ratio could be accounted for in terms of steric hindrance to approach by base to the C-8 hydrogen atom from the syn direction.

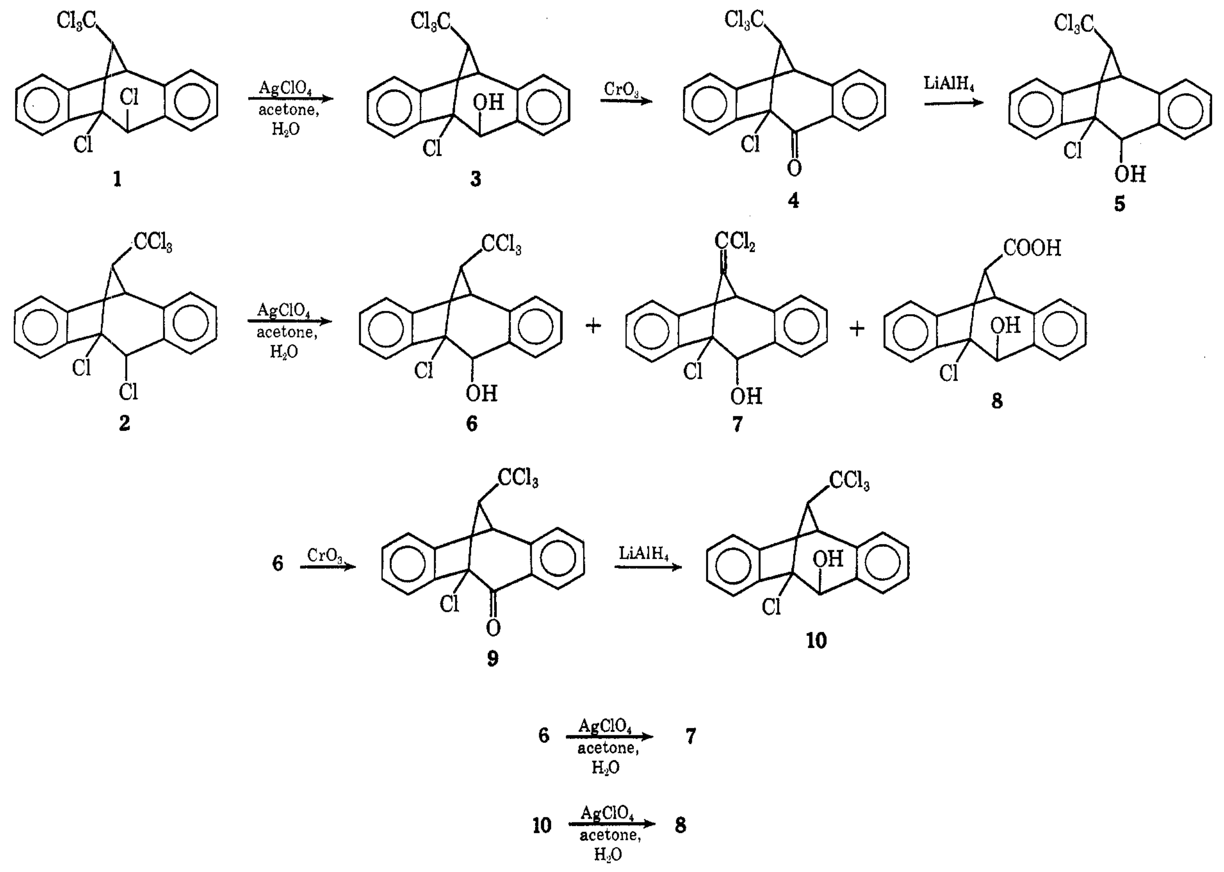
A great deal of data have been amassed on the variables associated with 1,2-elimination reactions.[2] Most of these data are concerned with how the nature of these reactions vary with changes either at the site of the leaving group (α and β positions) or in the base system employed. Little effort has been made to study what effect groups removed from the reaction sites (α and β) would have on the course of E2 eliminations. In particular, we wished to study the effect in β eliminations of groups removed from the reaction site in a sterically constrained system.

---

[1] (a) Taken in part from the M.S. thesis of J. P. Govoni, University of Maryland, 1970. (b) Presented in part at the 6th Middle Atlantic Regional Meeting of the American Chemical Society, Baltimore, Md., Feb 1971.

[2] (a) D. V. Banthorpe, "Elimination Reactions," Elsevier, Amsterdam, 1963; (b) J. F. Bunnett, *Angew. Chem., Int. Ed. Engl.*, **1**, 225 (1962); (c) R. F. Hudson, *Chimia (Aarau)*, **16**, 173 (1962); (d) D. J. McLennan, *Quart. Rev. (London)*, **21**, 490 (1967); (e) J. F. Bunnett, *Surv. Progr. Chem.*, **5**, 53 (1969).

SCHEME I



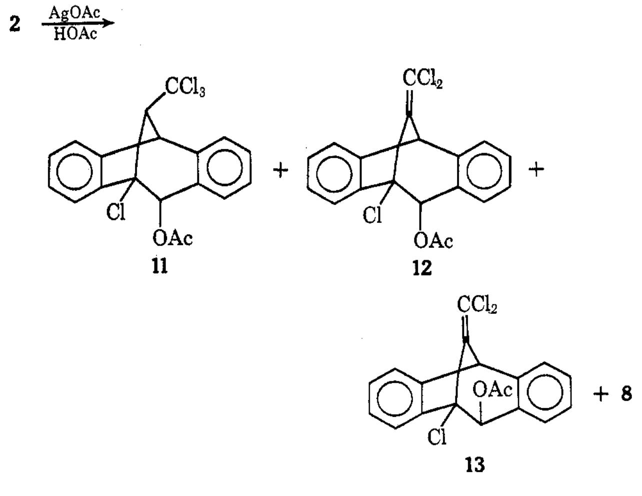
Results and Discussion

The epimeric trichloromethyl compounds (**1** and **2**) were available from a previous study.[3] These compounds appeared to be good candidates for studying the effect of substituents at the C-4 position on the rates of dehydrochlorination. Since the proton at C-8 is fixed in space with respect to the C-4 position, the electrostatic and/or steric effect of the groups at C-4 can be ascertained.

Scheme I outlines the syntheses of the alcohols and ketones whose rates of dehydrochlorination were measured.

Silver ion assisted solvolysis of **1** gives **3** cleanly. Oxidation of **3** to ketone **4** goes smoothly as does the reduction of **4** (lithium aluminum hydride) to give the endo alcohol **5**. However, solvolysis of the chloride **2** in aqueous acetone in the presence of an excess of silver perchlorate gives 60% **6**, 10% olefin **7**, and 30% acid **8**. Subsequently, it was shown that the endo alcohol **6** is converted slowly to the olefin **7** under the reaction conditions while the exo alcohol **10**[4] is converted very rapidly to the hydroxy acid **8**.

The rapid reaction of **10** with silver perchlorate in aqueous acetone (immediate precipitate of silver chloride is formed when aqueous silver perchlorate is mixed with **10** dissolved in aqueous acetone) is a clear example of neighboring-group participation in the solvolysis of the trichloromethyl group by an un-ionized hydroxyl group. It is felt that the hydroxyl group in **10** remains un-ionized during the course of these reactions for a number of reasons: (1) the presence of 0.1 *M* perchloric acid has no apparent effect on the rate of reaction of **10** or **6** with silver perchlorate in aqueous acetone; (2) **10** reacts only slowly with potassium carbonate in aqueous acetone and does not yield the acid **8**; (3) solvolysis of **2** with silver acetate in glacial acetic acid gives 20% endo acetate **11**, 55% *endo*-acetoxy olefin **12**, 20% of the acid **8** and ~5% of the *exo*-acetoxy olefin **13** (**11** → **12** under the reaction conditions). The transesterification of the acetate **12** yields the alcohol **7**. Formation of acid **8** presumably in-



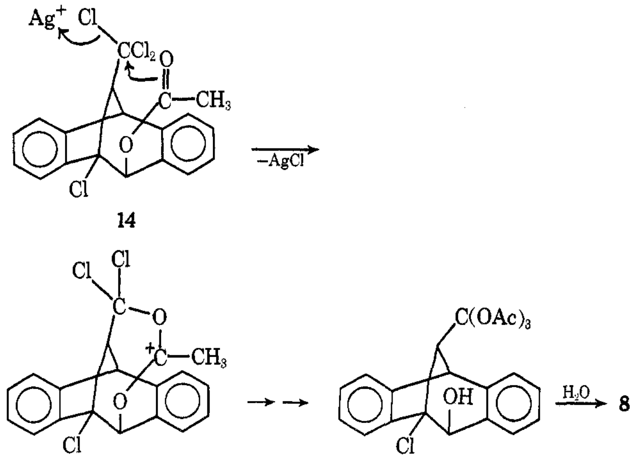
---

[3] B. B. Jarvis, J. P. Govoni, and P. J. Zell, *J. Amer. Chem. Soc.*, **93**, 913 (1971).

[4] The alcohol **10** is synthesized in high yield in two steps (see Scheme I) starting with **6**. Reduction of ketone **9** with lithium aluminum hydride occurs *via* hydride transfer from the sterically less hindered endo position.[3] The stereoelectronically more favored exo approach[5,6] is blocked by the bulky trichloromethyl group.

[5] (a) S. J. Cristol, F. P. Parungo, and D. E. Plorde, *J. Amer. Chem. Soc.*, **87**, 2870 (1965); (b) S. J. Cristol, R. J. Bopp, and A. E. Johnson, *J. Org. Chem.*, **34**, 3574 (1969).

[6] S. J. Cristol, F. P. Parungo, D. E. Plorde, and K. Schwarzenbach, *J. Amer. Chem. Soc.*, **87**, 2879 (1965).



volves participation by the *exo*-acetoxy group in the intermediate acetate **14**. Such participation by an acetoxy group is known to lead eventually to an alcohol if any water is present in the acetic acid.[7]

Interestingly, trichloromethylphenylcarbinol gives no reaction with silver perchlorate in aqueous acetone at reflux for extended periods of time. Normally, epoxides are formed less readily than tetrahydrofurans,[8,9] but the difference in reactivity between trichloromethylphenylcarbinol and **10** must be extremely large. This difference can be accounted for mainly in the entropy factor ($\Delta S^{\ddagger}$), since in **10** the hydroxyl group is held in close proximity to the incipient carbonium ion owing to the rigidity of the carbon skeletal system.

What is less clear, though, is why a number of these *syn*-trichloromethyl compounds (**6** and **11**) undergo loss of hydrogen chloride upon treatment with silver perchlorate in aqueous acetone. The *anti*-trichloromethyl epimeric alcohols **3** and **5** and 2,2-bis(4-chlorophenyl)-1,1,1-trichloroethane (DDT) show no sign of reacting with silver perchlorate under these conditions. The syn ketone **9** also reacts, albeit slowly, with silver perchlorate in refluxing aqueous acetone. It would appear that these reactions of **6**, **9**, and **11** are E1 reactions, but what is not clear is why the corresponding SN1 reactions, which normally accompany E1 reactions,[10,11] are not observed.

The trichloromethyl compounds react with a variety of bases with loss of hydrogen chloride to give the corresponding dichloromethylene compounds (**7**, **15**, and **16**). However, the olefins are sensitive to strong base,[13] and it was most convenient to use the relatively mild base system, lithium chloride in dimethylacetamide (DMA), for both syntheses and kinetic studies.

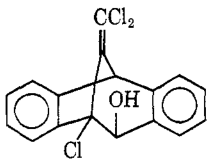
TABLE I

RATE DATA[a] FOR LOSS OF HYDROGEN CHLORIDE FOR THE TETRACHLORIDES **3**, **4**, **5**, **6**, **9**, AND **10**[b] WITH LITHIUM CHLORIDE[c,d] IN DMA AT 130.2°

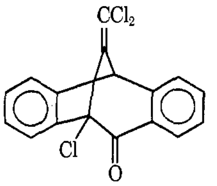
Compd	k_2 (l. mol^{-1} sec^{-1})[e]	k^{rel}
anti-**4** (ketone)	7.0×10^{-5}	50
anti-**3** (*exo*-OH)	5.6×10^{-6}	4.0
anti-**5** (*endo*-OH)	1.4×10^{-6}	1.0
syn-**9** (ketone)	3.4×10^{-3}	2400
syn-**10** (*exo*-OH)	3.2×10^{-3}	2300
syn-**6** (*endo*-OH)	3.2×10^{-3}	2300

[a] Reaction rates were followed by titration with standard base for liberated acid. [b] 0.03 *M*. [c] 0.308 *M*. [d] Reactions were first order in chloride ion as shown by a linear plot of k_{obsd} *vs.* [Cl⁻], where [Cl⁻] varied from 0.902 to 0.094 *M*. [e] Precision of ±2–4% for k_2.

Table I gives the rate data for dehydrochlorination of the tetrachlorides with lithium chloride in DMA at 130.2°.



15



16

The behavior of the anti epimers (**3**–**5**) can be contrasted to that of the syn compounds (**6**, **9**, and **10**). Whereas the reactivities of the syn isomers (**6**, **9**, and **10**) toward lithium chloride in DMA are all about the same, the reactivities of the anti epimers vary by a factor of 50 going from the endo alcohol **5** to the ketone **4**. This variation in rate for the anti series can be explained by the electronic nature of the substituent at C-4 (>C=O more electron withdrawing than the >CHOH group). Furthermore, this electrostatic effect appears to be transmitted through space (field effect[14]) rather than through the carbon chain.

The sensitivity of the elimination reactions in the *anti*-trichloromethyl compounds is also evident in compounds lacking the C-5 bridgehead chlorine atom. Five compounds in this series were synthesized as outlined below (Scheme II). Treatment of these trichlorides with lithium chloride in DMA gave the corresponding dichloro olefins (**25**–**29**) in high yields. Table II lists the rate data for the reactions of **18**–**22** with lithium chloride in DMA at 130.2°.

From a comparison of Tables I and II it is clear that the bridgehead chlorine atom in **3**–**5** has little effect on the behavior of these compounds in the elimination reactions. Furthermore, the effect of the substituents at C-4 on the rates of elimination (Table II) is that anticipated from the electron-withdrawing ability of these groups (>C=O > >CHOH > >CH₂).[15]

---

(7) S. Winstein, H. U. Hess, and R. E. Buckles, *J. Amer. Chem. Soc.*, **64**, 2796 (1942).

(8) B. Capon, *Quart. Rev. (London)*, **18**, 45 (1964).

(9) S. Winstein, E. Allred, R. Heck, and R. Glick, *Tetrahedron*, **3**, 1 (1958).

(10) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," 2nd Ed., Cornell University Press, Ithaca, N. Y., 1969, Chapter IX.

(11) Chlorine atoms are known[12] to have a stabilizing effect on carbon–carbon double bonds. This may account in part for high ratio of E1/SN1 products.

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

(13) Ketones **4** and **16** react instantly with 1.0 *M* potassium *tert*-butoxide in *tert*-butyl alcohol at room temperature to give a deep purple solution. No identifiable organic compounds could be isolated from these solutions. All of the 8-trichloromethyldibenzobicyclo[3.2.1]octadienes (and the corresponding olefins derived from these compounds) reported in this work behaved in a similar manner upon treatment with strong bases. The ketones were the most sensitive compounds.

(14) (a) R. Golden and L. M. Stock, *J. Amer. Chem. Soc.*, **88**, 5928 (1966); (b) C. F. Wilcox and C. Leung, *ibid.*, **90**, 336 (1968); (c) M. J. S. Dewar and A. P. Marchand, *ibid.*, **88**, 3318 (1966); (d) M. J. S. Dewar and T. G. Squires, *ibid.*, **89**, 210 (1967); (e) W. Adcock and M. J. S. Dewar, *ibid.*, **89**, 379 (1967); (f) C. L. Liotta, W. F. Fisher, and G. H. Green, *Chem. Commun.*, 1251 (1969).

(15) (a) The rate of elimination decreases going from **22** to *exo*-methoxy **21**, contrary to what might be expected from the electron-withdrawing ability of a methoxyl group compared with a hydrogen atom. The more bulky *exo*-methoxyl group may impede approach of base to the *syn*-C-8 proton. (b) The relatively large effect of the carbonyl group is consistent with the expected field effect; see P. G. Gassman and F. V. Zolar, *J. Amer. Chem. Soc.*, **88**, 3070 (1968), and R. M. Moriarty, C. R. Romain, and T. O. Lovett, *ibid.*, **89**, 3927 (1967).

SCHEME II

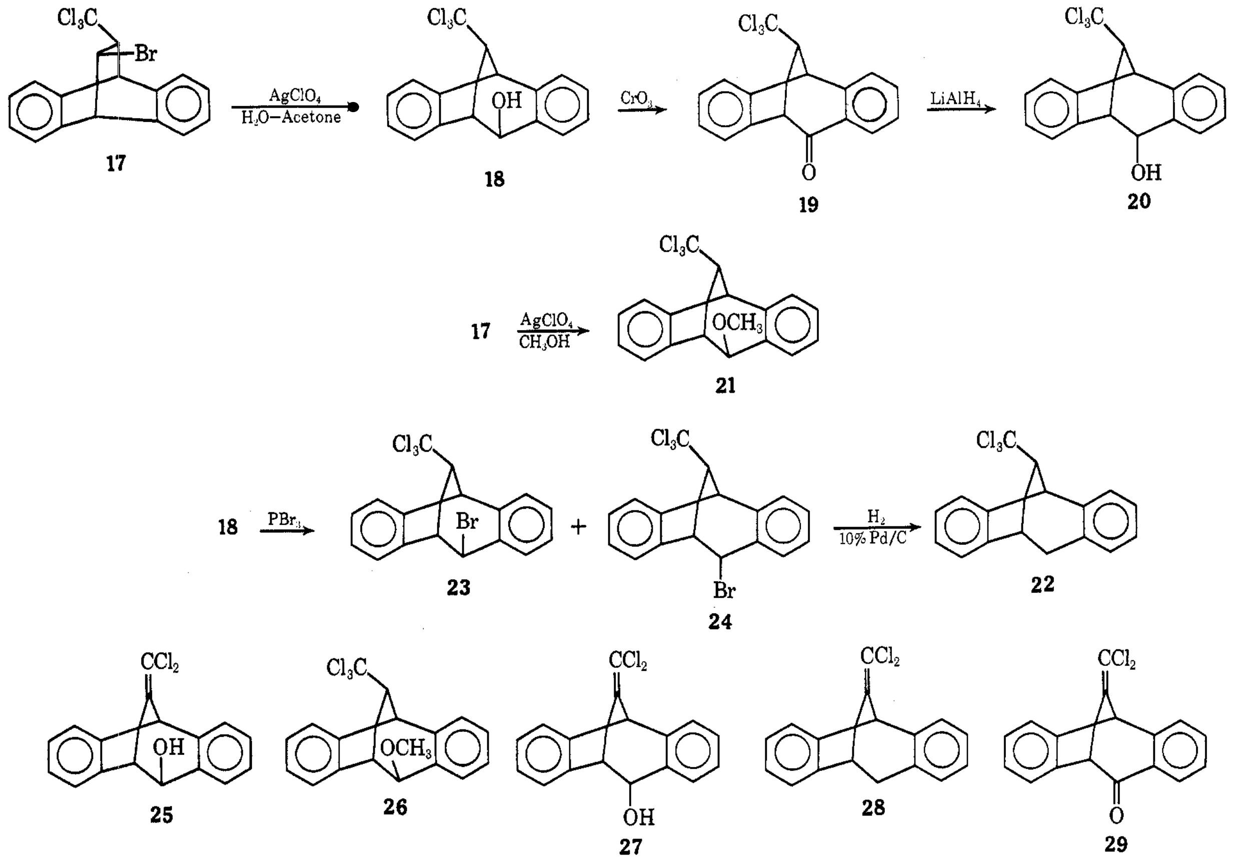


TABLE II

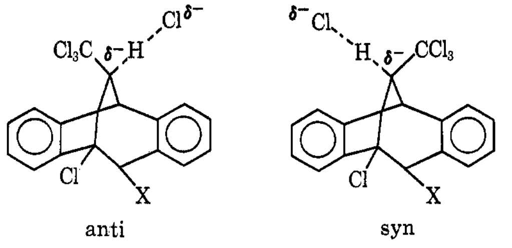
RATE DATA[a] FOR LOSS OF HYDROGEN CHLORIDE FOR THE TRICHLORIDES 18–22[b] WITH LITHIUM CHLORIDE[c,d] IN DMA AT 130.2°

Compd	k_2 (l. mol^{-1} sec^{-1})	k^{rel}
19	8.4×10^{-5}	65
18	6.8×10^{-6}	5.2
20	1.7×10^{-6}	1.3
22	1.3×10^{-6}	1.0
21	4.0×10^{-7}	0.33

[a] Reaction rates were followed by titration with standard base for liberated acid. [b] 0.03 *M*. [c] 0.308 *M*. [d] Reactions were first order in chloride ion as shown by a linear plot of K_{obsd} *vs.* [Cl$^-$], where [Cl$^-$] varied from 0.902 to 0.094 *M*.

Compounds **18**–**22** were also treated with potassium hydroxide in methanol at 65°. Attempts to obtain reproducible kinetic data past ~1 half-life for these reactions were unsuccessful presumably owing to significant product decomposition.[13] However, crude data (see Experimental Section) showed that the spread in reactivity (compared with data in Table II) between the methyl ether **21** and the ketone **19** had increased by a factor of only about 2.

The invariance in the rates of elimination in the *syn*-trichloromethyl ketone and alcohols (**6**, **9**, and **10**, Table I) can be contrasted with 50-fold range [k_4/k_5 (Table I) $\sim k_{19}/k_{20}$ (Table II) $= 50$] observed in the epimeric *anti*-trichloromethyl series. The difference can be attributed to a number of effects but again a simple field effect would appear to be most consistent with the data; *i.e.* in the transition state in the anti series (**3**, **4**, and **5**) a partial negative charge is being generated in the C–H bond situated directly over the C-4 position while in the transition state in the syn series (**6**, **9**, and **10**) the partial negative charge is developing in an area more removed from the substituents at C-4. This suggestion implies that for



anti   syn

these E2 eliminations the transition states lies somewhat toward the paenecarbanion[2e] extreme rather than exactly at the central position. Previous work with chloride ion initiated E2 eliminations in aprotic solvents[16] have suggested that such eliminations lie very close to the "central"[17] transition state; *i.e.*, a good deal of double bond character between C_α and C_β has already developed in the transition state. Recent work on hydrogen chloride elimination from meta- and para-substituted DDT with chloride ion in DMF has yielded a ρ of $+1.23$ for these eliminations,[18] indicating at least some negative charge buildup on the benzhydryl carbon (C_β). The ρ for such eliminations is considerably larger for the stronger base systems, *e.g.*, ethoxide ion in ethanol.[19] We observe only a modest increase in the spread of the relative rates in the *anti*-trichloromethyl series (**18**–**22**) going from chloride ion in DMA to hydroxide ion in methanol. There

(16) A. J. Parker, *Chem. Rev.*, **69**, 1 (1969).

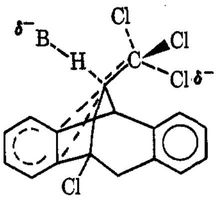
(17) E. Baciocchi and A. Schirali, *J. Chem. Soc. B*, 554 (1969).

(18) D. J. McLennan and R. J. Wong, *Tetrahedron Lett.*, 881 (1970).

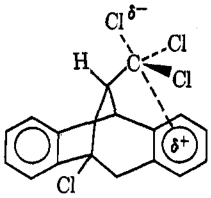
(19) S. J. Cristol, *J. Amer. Chem. Soc.*, **67**, 1494 (1945).

in fact may be a good deal of double-bond character developed in the transition state for loss of hydrogen chloride from these dibenzobicyclo[3.2.1]octadienes, but the data available do not require such a conclusion.[20]

The relatively large k_{syn}/k_{anti} ratios for these eliminations (Table I) may be due to a number of factors. One aspect that is often invoked in explaining rate differences is anchimeric assistance. Two different transition states (**30** and **31**) might be suggested which would account for the syn epimers' reacting more rapidly than the anti epimers. Both of these models can be rejected. **30** actually should be higher in energy than a transition state not involving participation of the benzene ring since **30** would represent an anti aromatic system;[21] **31** would suggest that the transition state would lie toward the paenecarbonium ion extreme[2e] a fact not in accord with experimental observations (*vide supra*). Furthermore, the anti benzene ring probably is more favorably disposed toward participation,[22] and, even if the syn benzene ring were oriented correctly for participation, evidence is available in analogous systems[23] to suggest that the reaction would still not make use of such participation.

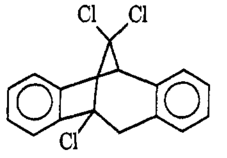


30

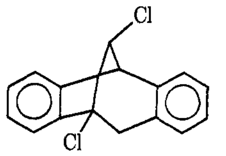


31

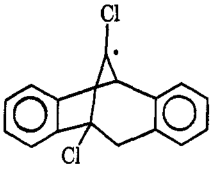
The most reasonable explanation for the large k_{syn}/k_{anti} ratio noted in Table I is the steric argument.[24] Reduction of the trichloride **32** with tri-*n*-butyltin hydride (n-Bu_3SnH) gives only the syn chloride **33**.[26] The product-determining step in this reaction is the chain transfer of a hydrogen atom from n-Bu_3SnH[27] to the radical **34**; this transfer takes place ~100% from the anti direction. Reduction of **32** with chromium(II) in aqueous DMF, a reaction believed to involve protonation of an intermediate carbanion as the product-determining step,[28a] also gives only **33**.[28b] Clearly, a variety of reagents prefer to approach the C-8 position in the dibenzobicyclo[3.2.1]octadiene system from the anti direction.[29]



32



33



34

Models show that reagents have a significantly more open approach from the anti direction than from the syn direction. Steric hindrance to attack by base from the syn direction then would seem to be the most reasonable explanation for the greater ease for E2 elimination of hydrogen chloride from the *syn*-8-trichloromethyldibenzobicyclo[3.2.1]octadienes in comparison with the anti epimers.[30]

Experimental Section[32]

Preparation of *exo*-4-Hydroxy-*anti*-8-trichloromethyldibenzobicyclo[3.2.1]octadiene (18).—To 10 g (0.025 mol) of **17**[33] dissolved in 100 ml of reagent grade acetone was added 10 g (0.048 mol) of silver perchlorate dissolved in 25 ml of water. The homogeneous mixture was stirred at reflux (65°) for 3 hr (a greenish yellow precipitate of silver bromide was formed). The mixture was allowed to cool, and 15 ml of concentrated hydrochloric acid was added to precipitate the excess silver ion. The inorganic precipitate was removed by filtration, water was added to the filtrate, and the filtrate was extracted twice with 100 ml of ether. The combined ether extracts were washed with water and saturated sodium carbonate solution and dried over anhydrous magnesium sulfate. The ether was removed by rotary evaporation, and a pmr spectrum of the resulting solid showed only the exo alcohol present. After recrystallization from Skellysolve B–carbon tetrachloride, the yield was 8.5 g (83%) of **18**, mp 159–160°, ν_{OH} 3590 cm^{-1}.

The pmr spectrum of **18** shows a singlet (1 H) at τ 5.68 ($J_{18} = 0$ Hz), two slightly broadened singlets (2 H and 1 H, respectively at 6.20 (H-5 and H-8 have the same chemial shift) and 6.53,[34] a doublet (1 H) at 5.37 ($J_{45} = 2.5$ Hz), and a complex multiplet (8 H) from 2.4 to 3.0.

Anal. Calcd for $C_{17}H_{13}Cl_3O$: C, 60.12; H, 3.86. Found: C, 59.87; H, 3.90.

Oxidation of 18 with Jones Reagent.—The alcohol **18** (8.0 g, 0.024 mol) was dissolved in 25 ml of reagent grade acetone and stirred at 25° under nitrogen. Jones reagent (15 ml, prepared from 26.72 g of chromium trioxide in 25 ml of concentrated sulfuric acid and diluted to 100 ml with water) was added dropwise over a 5-min period. Greenish chromium salts were seen to

---

[20] F. G. Bordwell, *Accounts Chem. Res.*, **3**, 281 (1970).

[21] R. Breslow, R. Pagni, and W. N. Washburn, *Tetrahedron Lett.*, 547 (1970); however, others have suggested that such an electronic array might be a source of stabilization. See C. K. Alden and D. I. Davies, *J. Chem. Soc. C*, 700 (1968).

[22] (a) S. J. Cristol, J. R. Mohrig, F. P. Parungo, D. E. Plorde, and K. Schwarzenbach, *J. Amer. Chem. Soc.*, **85**, 2675 (1963); (b) G. W. Klumpp, G. Ellen, and F. Bickelhaupt, *Recl. Trav. Chim. Pays-Bas*, **88**, 474 (1969).

[23] R. K. Bly and R. S. Bly, *J. Org. Chem.*, **31**, 1577 (1966).

[24] A number of studies[25] of E2 eliminations in bridged bicyclic systems has shown that elimination reactions in these systems are rather sensitive to steric hindrance.

[25] N. A. LeBel, P. D. Beirne, T. R. Karger, J. C. Powers, and P. M. Subramanian, *J. Amer. Chem. Soc.*, **85**, 3199 (1963); D. I. Davies and L. T. Parfitt, *J. Chem. Soc. C*, 2691 (1967).

[26] B. B. Jarvis and J. B. Yount, III, *Chem. Commun.*, 1405 (1969).

[27] (a) H. G. Kuivila, *Accounts Chem. Res.*, **1**, 299 (1968); (b) D. J. Carlsson and K. U. Ingold, *J. Amer. Chem. Soc.*, **90**, 7047 (1968).

[28] (a) J. K. Kochi and J. W. Powers, *ibid.*, **92**, 137 (1970); (b) J. B. Yount, III, M.S. Thesis, University of Maryland, 1970.

[29] The C-8 anti chlorides solvolyze much more readily than do the epimeric syn chlorides;[22a] however, these reactions are not comparable with those reported above since solvolysis of the anti chlorides leads to carbon skeletal rearranged products.

[30] Torsional strain[25,31] might also be envoked to account for the rate differences observed in these epimers. However, contribution by torsional strain is believed to be minimal in the formation of exocyclic double bonds.[31c]

[31] (a) C. L. Osborn, J. V. Van Auken, and D. J. Treker, *J. Amer. Chem. Soc.*, **90**, 5806 (1968); (b) F. R. Jensen, J. H. Gale, and J. E. Rogers, *ibid.*, **90**, 5739 (1968); (c) P. v. R. Schleyer, *ibid.*, **89**, 701 (1967).

[32] Melting points were determined on a Fisher-Johns apparatus and are uncorrected. Pmr spectra were run in carbon tetrachloride solutions (unless otherwise noted) and measured with a Varian A-60D spectrometer with tetramethylsilane (τ 10.00) as the internal standard. J values are "observed" ones. Ir spectra were taken on a Perkin-Elmer 337 infrared spectrometer in 0.5-mm matched cells with carbon tetrachloride as the solvent. The uv spectra of **3** and **4** were obtained on a Cary 15 spectrometer in 1.0-mm matched quartz cells with ethanol as the solvent. Microanalyses were performed by Dr. F. K. Kasler, University of Maryland.

[33] B. B. Jarvis, *J. Org. Chem.*, **33**, 4075 (1968).

[34] Since the chemical shift associated with the hydroxyl group does not remain constant when the concentration of the compound in solution is changed, this peak is not reported for the other alcohols (**3**, **5**, **6**, **7**, **8**, **10**, **15**, **20**, **25**, and **27**.

precipitate. The reaction solution was allowed to stir for an additional 5 min at which time 75 ml of water was added to dissolve the chromium salts and the entire mixture was extracted twice with 50-ml portions of ether. The ethereal portions were washed with saturated sodium chloride and dried over anhydrous magnesium sulfate. The ether was removed by rotary evaporation, and the resulting solid was found to be entirely the *anti*-8-trichloromethyldibenzobicyclo[3.2.1]octadien-4-one (**19**) by pmr spectroscopy. Recrystallization from a methanol–methylene chloride mixture gave 6.0 g (75%) of ketone: mp 155–156°; $\nu_{C=O}$ 1750 cm^{-1}; λ 211 nm (ε 24,700), 227 (14,300), 242 (12,300), 278 (2750), 300 (1200), 338 (400), 351 (340) and 365–370 (160).

The pmr spectrum of **19** shows a singlet (1 H) at τ 6.06, a pair of doublets (1 H each) at 5.42 and 5.58 (J_{15} = 1.4 Hz, long range coupling;[35] J_{18} = 0 Hz), and a complex multiplet from 2.2 to 3.0.

Anal. Calcd for $C_{17}H_{11}Cl_3O$: C, 60.48; H, 3.28. Found: C, 60.78; H, 3.38.

Preparation of *endo*-4-Hydroxy-*anti*-8-trichloromethyldibenzobicyclo[3.2.1]octadiene (20).—To 100 mg (2.6 mmol) of lithium aluminum hydride dissolved in 15 ml of dry ether at room temperature and under nitrogen was slowly added 1.4 g (4.1 mmol) of the ketone **19** as a solid. The mixture was stirred for an additional 5 min at which point water was added dropwise to destroy the excess lithium aluminum hydride. The inorganic precipitate which formed was removed by filtration, and water was added to the filtrate. Two 50-ml ether extractions were taken, and the combined ethereal portions were washed with water and saturated sodium chloride and dried over magnesium sulfate. Rotary evaporation of the solvent yielded a yellow oil whose pmr spectrum showed only the endo alcohol **20** present. This was crystallized from a pentane–carbon tetrachloride mixture to give 1.2 g (86%) of **20**, mp 150–151°.

The pmr spectrum for **20** shows two singlets (1 H each) at τ 5.72 and 6.67 (J_{18} = 0 Hz), two doublets (1 H each) at 5.28 and 6.17 (J_{45} = 5.6 Hz), and a complex multiplet (8 H) from 2.3 to 3.0.

Anal. Calcd for $C_{17}H_{13}Cl_3O$: C, 60.12; H, 3.86. Found: C, 60.08; H, 3.93.

Preparation of *exo*-4-Methoxy-*anti*-8-trichloromethyldibenzobicyclo[3.2.1]octadiene (21).—To a solution of 4.5 g (0.011 mol) of **17** in 100 ml of absolute methanol, held at reflux, was added 4.5 g (0.022 mol) of silver perchlorate dissolved in 25 ml of methanol. The mixture was held at reflux for 3 hr and cooled, and 150 ml of water was added. Two 100-ml ether extractions were taken, and the combine ethereal portions were washed with water and saturated with sodium chloride and dried over magnesium sulfate. Rotary evaporation of the ether yielded a solid, which was found by pmr spectroscopy to be the *exo*-methoxy compound **21**. This was recrystallized from ethanol to yield 3.6 g (79%) of **21**, mp 114–115°.

The pmr spectrum of **21** shows three singlets (1 H, 1 H, and 3 H, respectively) at τ 5.90 (J_{45} < 0.5 Hz), 6.15 (J_{18} = 0 Hz), and 6.36 (OCH_3), a pair of broadened overlapping singlets (2 H) from 5.67 to 5.75, and a complex multiplet (8 H) from 2.5 to 3.0.

Anal. Calcd for $C_{18}H_{15}Cl_3O$: C, 61.13; H, 4.28. Found: C, 61.15; H, 4.34.

Reaction of 18 with Phosphorus Tribromide.—To 3.0 g (8.9 mmol) of the exo alcohol **18**, dissolved in 20 ml of dry ether, was added a solution of 10 ml of phosphorus tribromide and 5 ml of dry ether. The mixture was held at reflux for 15 hr. The excess phosphorus tribromide was destroyed by slow addition of saturated sodium carbonate. Water was added, and two 50-ml ether extracts were taken. The combined ethereal portions were washed with saturated sodium carbonate and water, dried over magnesium sulfate, and decolorized with charcoal. The ether was removed by rotary evaporation to yield a yellow oil (2.9 g, 81%). A pmr spectrum showed approximately 60% exo bromide **23** and 40% an isomer believed to be the endo bromide **24**. Slow crystallization of the mixture from ethanol gave 0.4 g of pure exo compound **23**, mp 125–126°. A second recrystallization gave 2.3 g of a 50:50 mixture of the isomers. An attempt to isolate the endo isomer by chromatography on silica gel gave no separation. No further attempts were made since the bromide was an intermediate in the synthesis of the hydrocarbon described next.

The pmr spectrum for **23** shows two singlets (1 H each) at τ 5.68 and 5.90, a pair of doublets (1 H each) at τ 4.56 and 5.82 (J_{45} = 2.2 Hz), and a complex multiplet (8 H) from τ 2.4 to 30.

Anal. Calcd for $C_{17}H_{12}BrCl_3$: C, 50.72; H, 3.01. Found: C, 50.48; H, 3.02.

Preparation of *anti*-8-Trichloromethyldibenzobicyclo[3.2.1]-octadiene (22).—One gram (2.5 mmol) of a 50:50 mixture of exo and endo bromides **23** and **24**, dissolved in 35 ml of absolute ethanol was placed in a hydrogenation apparatus[36] with 200 mg of 10% palladium on charcoal as a catalyst. After 2 hr, addition of hydrogen had ceased with 65.0 ml of hydrogen gas consumed by the ethanol solution. Removal of the catalyst by filtration was followed by addition of water and two extractions with 50-ml portions of ether. The ethereal portions were washed with saturated sodium chloride and dried over magnesium sulfate. Removal of the ether by rotary evaporation resulted in a solid whose pmr spectrum indicated that it was pure hydrocarbon **22**. Recrystallization from ethanol gave 0.58 g (71%) of **22**, mp 152°.

The pmr spectrum of **22** shows two singlets (1 H each) at τ 5.73 and 6.57 (J_{18} = 0 Hz), two doublet of doublets (1 H each) at 6.63 (J_{gem} = 17.0 Hz; $J_{exo\text{-}45}$ = 1.7 Hz) and 7.18 (J_{gem} = 17.0 Hz; $J_{endo\text{-}45}$ = 5.0 Hz), a complex multiplet (1 H) from 6.06 to 6.22, and another complex multiplet (8 H) from 2.8 to 3.1.

Anal. Calcd for $C_{17}H_{13}Cl_3$: C, 63.09; H, 4.05. Found: C, 62.80; H, 4.11.

Dehydrochlorination of 18–22.—Treatment of the trichlorides **18–22** with 1 *M* lithium chloride in dimethylacetamide (DMA) at 130° gave the corresponding olefins **25–29**. Reaction times varied from 1 hr for the ketone **19** to 10 days for the methyl ether **21**. Reaction mixtures were worked up by quenching with water followed by ether extraction. The products were isolated in 75–90% yield and the materials were recrystallized from ethanol. Pertinent physical data for **25–29** are given below. Treatment of **18–22** with 1 *M* potassium *tert*-butoxide in *tert*-butyl alcohol at reflux gave **26** and **28** in moderately good yields (50–70%), and **25** and **27** in poor yields (5–10%). **29** could not be observed in the reaction of **19** with this base system. Under the conditions of the reaction (1 *M* base at room temperature), **29** was rapidly destroyed. The other olefins (**25–28**) were also slowly destroyed under these conditions.

The pmr spectrum of **25** (mp 146–147°; $\nu_{C=C}$ 1660 cm^{-1}, ν_{OH} 3580 cm^{-1}) shows two singlets (1 H and 2 H, respectively) at τ 5.46 and 5.38 (H-4 and H-5 have the same chemical shift) and a complex multiplet from 2.3 to 3.0.

Anal. Calcd for $C_{17}H_{12}Cl_2O$: C, 67.35; H, 3.99. Found: C, 67.40; H, 4.06.

The pmr spectrum for **26** (mp 156–157°; $\nu_{C=C}$ 1655 cm^{-1}, $\nu_{C=O}$ 1090 cm^{-1}) shows two singlets (1 H and 3 H, respectively) at τ 5.38 (J_{18} = 0 Hz) and 6.39 (OCH_3), a multiplet (2 H) from 5.55 to 5.70, and another multiplet (8 H) from 2.3 to 3.0.

Anal. Calcd for $C_{18}H_{14}Cl_2O$: C, 68.16; H, 4.45. Found: C, 68.06; H, 4.53.

The pmr spectrum of **27** (mp 131–132°; $\nu_{C=C}$ 1645 cm^{-1}, ν_{OH} 3570 cm^{-1}) shows a singlet (1 H) at τ 5.43, a pair of doublets (1 H each) at 5.10 and 5.72 (J_{45} = 5.8 Hz), and a complex multiplet from 2.3 to 3.0.

Anal. Calcd for $C_{17}H_{12}Cl_2O$: C, 67.35; H, 3.99. Found: C, 67.10; H, 4.06.

The pmr spectrum of **28** (mp 148–149°, $\nu_{C=C}$ 1650 cm^{-1}) shows a singlet (1 H) at τ 5.40, a pair of doublet of doublets (1 H each) at 6.61 (J_{gem} = 17.0, $J_{exo\text{-}45}$ = 1.6 Hz) and 7.17 (J_{gem} = 17.0; $J_{endo\text{-}45}$ = 5.0 Hz), a complex multiplet (1 H) from 5.72 to 5.88, and another complex multiplet (8 H) from 2.7 to 3.0.

Anal. Calcd for $C_{17}H_{12}Cl_2$: C, 71.10; H, 4.21. Found: C, 70.99; H, 4.27.

The pmr spectrum for **29** [mp 153–154°; $\nu_{C=C}$ 1650 cm^{-1}, $\nu_{C=O}$ 1700 cm^{-1}; λ 208 nm (ε 36,300), 223 (31,600), 262–272 (4440), 295–308 (760), 340 (410), 355 (380), 372 (180)] shows two singlets (1 H each) at τ 5.15 and 5.27 and a complex multiplet (8 H) from 2.2 to 3.0.

Anal. Calcd for $C_{17}H_{10}Cl_2O$: C, 67.80; H, 3.34. Found: C, 67.52; H, 3.52.

Preparation of *exo*-4-Hydroxy-5-chloro-*anti*-8-trichloromethyldibenzobicyclo[3.2.1]octadiene (3).—To a solution of 2.0 g (5.1 mmol) of anti-exo chloride **1**[3] in 30 ml of acetone, held at reflux, was added 1.6 g (7.8 mmol) of silver perchlorate dissolved in 15 ml of water. The homogeneous mixture was held at reflux (65°) for 6 hr and worked up as usual. (The reaction was in-

---

(35) S. J. Cristol, J. R. Mohrig, and D. E. Plorde, *J. Org. Chem.*, **30**, 1956 (1965).

(36) K. B. Wiberg, "Laboratory Technique in Organic Chemistry," McGraw Hill, New York, N. Y., 1960, p 228.

complete after 4 hr.) Recrystallization from Skellsolve B–ether gave 1.6 g (87%) of the alcohol **3**, mp 158–159°, ν_{OH} 3650 cm^{-1}.

The pmr spectrum of **3** shows three singlets (1 H each) at τ 5.32, 5.34, and 5.80 (J_{18} = 0 Hz) and a complex multiple (8 H) from 2.3 to 3.0.

Anal. Calcd for $C_{17}H_{12}Cl_4O$: C, 54.58; H, 3.23. Found: C, 54.77; H, 3.30.

Preparation of 5-Chloro-*anti*-8-trichloromethyldibenzobicyclo[3.2.1]octadien-4-one (4).—To 2.2 g (0.059 mol) of alcohol **3** dissolved in 15 ml of acetone under nitrogen was slowly added 7 ml of Jones reagent at 25°. The rest of the procedure is like that for the preparation of **19**. The yield was 2.0 g (91%) of **4**, mp 195° (from ethanol), $\nu_{C=O}$ 1702 cm^{-1}.

The pmr spectrum for **4** shows two singlets (1 H each) at τ 4.98 and 5.87 (J_{18} = 0 Hz) and a complex multiplet (8 H) from 2.1 to 3.0.

Preparation of *endo*-4-Hydroxy-5-chloro-*anti*-8-trichloromethyldibenzobicyclo[3.2.1]octadiene (5).—To 90 mg (2.5 mmol) of lithium aluminum hydride dissolved in 15 ml of dry ether under nitrogen at room temperature was added slowly 1.0 g (2.7 mmol) of ketone **4** as a solid. The rest of the procedure is like that for the preparation of **20**. The yield was 0.82 g (82%) of pure **5**, mp 179° (Skellysolve B–ether), ν_{OH} 3550 cm^{-1}.

The pmr spectrum for **5** shows three singlets (1 H each) at τ 4.98, 5.34, and 6.32 (J_{18} = 0 Hz) and a complex multiplet (8 H) from 2.4 to 3.0.

Anal. Calcd for $C_{17}H_{12}Cl_4O$: C, 54.58; H, 3.23. Found: C, 54.34; H, 3.30.

Reaction of *endo*-4,5-Dichloro-*syn*-8-trichloromethyldibenzobicyclo[3.2.1]octadiene (2) with Silver Perchlorate in Aqueous Acetone.—To 2.0 g (5.1 mmol) of **2**[3] in 30 ml of acetone was added 2.4 g (11.7 mmol) of silver perchlorate in 15 ml of water. The homogeneous mixture was held at reflux (65°) for 6 hr. After the solution was allowed to cool, concentrated hydrochloric acid was added, and the silver chloride was removed by filtration. The remaining procedure was identical with that used for the preparation of **18**. Removal of the ether by rotary evaporation yielded an oil, but addition of 10 ml of carbon tetrachloride resulted in the formation of a precipitate. The insoluble material (0.45 g) was collected, and a pmr spectrum of the *filtrate* was taken. This revealed a mixture of 85% **6** and 15% **2**. The total weight of the mixture as an oil was 1.15 g. The oil was crystallized from Skellysolve B–ether to give 0.91 g (48%) of **6**, mp 149–150°, ν_{OH} 3555 cm^{-1}.

The pmr spectrum of **6** shows a singlet (1 H) at τ 4.54, a pair of doublets (1 H each) at 5.50 and 5.86 (J_{18} = 3.6 Hz), and a complex multiplet (8 H) from 2.4 to 3.0.

Anal. Calcd for $C_{17}H_{12}Cl_4O$: C, 54.58; H, 3.23. Found: C, 54.30; H, 3.27.

The solid which was collected was found to be soluble in saturated sodium carbonate solution, and an ir spectrum of this solid (KBr pellet) showed the unknown substance to be an acid. After two recrystallizations from acetic acid–water, 0.20 g (13%) of **8** was obtained, mp 286–287°, ν_{OH} 3550 cm^{-1}.

The pmr spectrum of **8** [in $CD_3S(=O)CD_3$] shows a singlet (1 H) at τ 4.42, a pair of doublets (1 H each) at 5.62 and 6.20 (J_{18} = 4.5 Hz), and a complex multiplet (8 H) from 2.3 to 3.0.

Anal. Calcd for $C_{17}H_{13}ClO_3$: C, 67.89; H, 4.36. Found: C, 67.59; H, 4.47.

It was found that the reaction of **2** with silver perchlorate did not proceed when stirred at room temperature for 4 hr. The reaction of **2** with silver perchlorate in aqueous acetone that was 0.1 *M* in perchloric acid gave essentially identical results as the reaction run in the absence of perchloric acid. Also, addition of potassium carbonate (forming a basic solution) slowed the reaction (50% completion after a 20-hr reflux period with 2 equiv of silver perchlorate to 1 equiv of potassium carbonate).

Preparation of 5-Chloro-*syn*-8-trichloromethyldibenzobicyclo[3.2.1]octadien-4-one (9).—The alcohol **6** (0.80 g, 2.2 mmol) was dissolved in 10 ml of acetone under nitrogen. Jones reagent (5 ml) was added and the reaction was run in the same manner as described previously. The yield was 0.71 g (89%) of ketone **9**, mp 182–183° (from ethanol–methylene chloride), $\nu_{C=O}$ 1710 cm^{-1}.

The pmr spectrum of **9** shows a pair of doublets (1 H each) at τ 5.25 and 5.42 (J_{18} = 3.7 Hz) and a complex multiplet (8 H) from 2.1 to 3.0.

Anal. Calcd for $C_{17}H_{10}Cl_4O$: C, 54.88; H, 2.69. Found: C, 54.89; H, 2.81.

Preparation of *exo*-4-Hydroxy-5-chloro-*syn*-8-trichloromethyldibenzobicyclo[3.2.1]octadiene (10).—The ketone **9** (0.60 g, 1.6 mmol) was added slowly as a solid to 50 mg (1.3 mmol) of lithium aluminum hydride in 15 ml of dry ether. The procedure for the preparation of **20** was followed, and the resulting oil was crystallized from pentane–ether to give 0.55 g (92%) of the exo alcohol **10**, mp 128°, ν_{OH} 3555 cm^{-1}.

The pmr spectrum of **10** shows a singlet at τ 5.41, a pair of doublets (1 H each) at 5.43 and 5.92 (J_{18} = 3.5 Hz), and a complex multiplet (8 H) from 2.3 to 3.0.

Anal. Calcd for $C_{17}H_{12}Cl_4O$: C, 54.58; H, 3.23. Found: C, 54.52; H, 3.32.

Reaction of the Four 4-Hydroxy-5-chloro-8-trichloromethyldibenzobicyclo[3.2.1]octadienes (3, 5, 6, and 10) with Silver Perchlorate in Aqueous Acetone.—To 0.200 g (0.54 mmol) of each of the alcohols dissolved in 20 ml of acetone was added 0.350 g (1.69 mmol, 3 equiv) of silver perchlorate dissolved in 10 ml of water. The mixture was held at reflux for the time specified below, and the solution was allowed to cool. Hydrochloric acid was added, and the inorganic precipitate was removed by filtration. The filtrate after addition of water was extracted with two 50-ml portions of ether. The combined ethereal portions were washed three times with saturated sodium carbonate solution, dried over magnesium sulfate, and rotary evaporated. The resulting oil was dissolved in carbon tetrachloride solution and a pmr spectrum was taken. The three sodium carbonate washings and the aqueous layer were combined, made acidic with hydrochloric acid, and extracted twice with 100-ml portions of ether. The ethereal portions were washed with saturated sodium chloride, dried over magnesium chloride, and rotary evaporated. The following results were obtained.

For **3** and **5** (after 48 hr), only starting material was observed in the initial ether layer, and no organic material was found in the ether extracts of the aqueous layer.

For **6** (after 24 hr), 60% **7** was found present in the ether layer, and no acid was observed in the aqueous layer. Reflux of the recovered material for another 30 hr under the same conditions resulted in complete conversion of **6** to **7**. The oil was crystallized from Skellysolve B–ether to give 0.125 g (69%) of pure **7**, mp 147–148°, $\nu_{C=C}$ 1640 cm^{-1}, ν_{OH} 3650 cm^{-1}.

The pmr spectrum of **7** shows two singlets (1 H each) at τ 4.92 and 5.17 and a complex multiplet (8 H) from 2.4 to 3.0.

Anal. Calcd for $C_{17}H_{11}Cl_3O$: C, 60.48; H, 3.28. Found: C, 60.50; H, 3.39.

For **10**, instantaneous precipitation of silver chloride was observed when the silver perchlorate was added to the acetone solution of **10** at room temperature. After a 30-min period of reflux, the reaction was worked up to yield no material in the ether layer and 0.120 g (75%) of acid **8** from the water layer (recrystallization from acetic acid–water). The structure was proven by ir spectroscopy and a mixture melting point with an analytical sample of **8**.

Reaction of Syn-Endo Chloride 2 with Silver Acetate in Glacial Acetic Acid.—A mixture of 2.5 g (6.4 mmol) of **2** and 2.0 g (12 mmol) of silver acetate in 50 ml of glacial acetic acid was held at reflux for 19 hr. At this time most of the glacial acetic acid was removed by distillation, the silver chloride removed by filtration, and water added to the filtrate. After two extractions with 100-ml portions of ether, the combined extracts were washed three times with saturated sodium carbonate and dried over magnesium sulfate. Removal of the ether by rotary evaporation resulted in an oil that was found (by pmr spectroscopy) to consist of 25% acetate **11**, 70% olefin **12**, and 5% olefin **13** (configuration not actually proven). The oil weighed 1.9 g.

The aqueous layers were combined, made acidic, and worked up with ether to give 0.5 g of the acid **8** (structure confirmed by mixture melting point and ir spectroscopy after recrystallization from acetic acid–water). The oil (*vide supra*) was recrystallized from pentane and then recrystallized from methanol to give 0.640 g of **12**: mp 190°; $\nu_{C=C}$ 1640 cm^{-1}, $\nu_{C=O}$ 1690 cm^{-1}, ν_{C-O} 1220 cm^{-1}). Further fractional crystallizations from pentane and methanol failed to separate the remaining olefin **12** from the acetate **11** and from the unconfirmed olefin **13**.

The pmr spectrum of **12** shows three singlets (1 H, 1 H, and 3 H, respectively) at τ 4.12, 5.16, and 7.84 [$OC(=O)CH_3$], and a complex multiplet (8 H) from 2.3 to 3.0.

Anal. Calcd for $C_{19}H_{13}Cl_3O$: C, 60.11; H, 3.46. Found: C, 60.19; H, 3.53.

Treatment of the Acetoxy Olefin 12 with Hydrochloric Acid in Methanol.—A solution of 0.50 g (1.3 mmol) of **12** in 25 ml of concentrated hydrochloric acid was held at reflux for 7 hr. Water was then added, and two 50-ml ether extractions were taken. The extracts were combined and washed with saturated sodium chloride, dried over magnesium sulfate, and decolorized with charcoal. Removal of the ether by rotary evaporation resulted in an oil, whose pmr spectrum was identical with that of the hydroxy olefin **7**. Crystallization from pentane–ether gave 0.41 g (93%), mp 188–190°.

Reaction of Trichloromethylphenylcarbinol with Silver Perchlorate in Aqueous Acetone.—To 2.0 g (0.16 mol) of trichloromethylphenylcarbinol[37] dissolved in 60 ml of acetone was added 3 equiv (10.0 g) of silver perchlorate in 30 ml of water to form a homogeneous solution. No silver chloride precipitate was observed during a 36-hr period of reflux. Work-up gave only unreacted starting material.

Reaction of DDT with Silver Perchlorate in Aqueous Acetone.—2,2-Bis(4-chlorophenyl)-1,1,1-trichloroethane (DDT, 1 g, 2.8 mmol) in 20 ml of acetone was heated to reflux. To this was added 1.75 g (8.4 mmol) of silver perchlorate in 10 ml of water, and the refluxing was continued for 48 hr. The standard work-up revealed only starting material in the ether layer and only traces of unidentifiable material in the water layer.

Reaction of the Syn Ketone 9 with Silver Perchlorate in Aqueous Acetone.—A solution of 0.20 g (0.54 mmol) of **9** and 0.34 g (16.2 mmol) of silver perchlorate in 20 ml of acetone and 10 ml of water was held at reflux for 48 hr. The reaction was worked up in the usual manner. The ether layer showed that ~10% of the ketone had reacted to give the corresponding olefin (*vide infra*). The aqueous layer yielded no organic material.

Synthesis of Olefins 15 and 16.—Olefins **15** and **16** were synthesized from **10** and **9**, respectively, in the same fashion (1 *M* lithium chloride in DMA at 130°) as in the case of the olefins **25** and **29** (*vide supra*). The olefins were obtained in 80–90% and were recrystallized from ethanol.

The pmr spectrum for the olefin **15** (mp 169°; $\nu_{C=C}$ 1650 cm^{-1}, ν_{OH} 3560 cm^{-1}) shows two singlets (1 H each) at τ 5.15 and 5.36 and a complex multiplet (8 H) from 2.3 to 3.0.

Anal. Calcd for $C_{17}H_{11}Cl_3O$: C, 60.48; H, 3.28. Found: C, 60.24; H, 3.36.

The pmr spectrum of the ketone **16** (mp 200°; $\nu_{C=C}$ 1620 cm^{-1}, $\nu_{C=O}$ 1690 cm^{-1}) shows a singlet (1 H) at τ 4.85 and a complex multiplet (8 H) from 2.2 to 3.0.

Anal. Calcd for $C_{17}H_9Cl_3O$: C, 60.84; H, 2.73. Found: C, 60.95; H, 2.81.

Kinetic Procedure.—Dimethylacetamide (reagent grade and twice distilled *in vacuo* from P_2O_5) solution (0.03 *M* in alkyl halide and 0.308 *M* in lithium chloride, standardized against silver nitrate by potentiometric titration) was placed in sealed ampoules and heated at 130.2° (±0.05°) in a constant temperature silicone oil bath. Samples (5.0 ml) were withdrawn at varying times and quenched in 50 ml of water. The solutions were analyzed by potentiometric titration (Sargent–Welch Model DG recording titrator) against a standardized solution of sodium hydroxide. A plot of log (liberated acid) *vs.* time gave a straight line, the slope of which was $k_{obsd}/2.303$. The second-order rate constant (k_2) is $k_{obsd}/[Cl^-]$. By variation of [LiCl] from 0.902 to 0.094 *M*, it was shown that each run gave the same k_2 to within ±10%.

Attempts at accurately measuring the rates of reactions of the alkyl halides (0.03 *M*) with 0.312 *M* sodium hydroxide in methanol at 65.1° (sealed ampoules) were not successful. Plots of log (liberated Cl^-) *vs.* time gave fairly straight lines for only ~20–40% reaction times. Rough data on the relative half-lives of the reactions of **18**–**22** with 0.312 *M* sodium hydroxide in methanol at 65.1° were obtained by quenching the reactions at ~15, 25, and 40% reaction times and measuring the extent of reaction by pmr spectroscopy. The relative rates for disappearance of starting materials as measured in this fashion follow: hydrocarbon **22** (1.0), methyl ether **21** (0.4), endo alcohol **20** (1.5), exo alcohol **18** (8), ketone **19** (150).

Registry No.—**3**, 27995-04-6; **4**, 27995-05-7; **5**, 27948-20-5; **6**, 27948-21-6; **7**, 34226-23-8; **8**, 34226-24-9; **9**, 27948-22-7; **10**, 34226-26-1; **12**, 34226-27-2; **15**, 34226-28-3; **16**, 34220-44-5; **18**, 34226-29-4; **19**, 34226-30-7; **20**, 34226-31-8; **21**, 34226-32-9; **22**, 34226-33-0; **23**, 34226-34-1; **25**, 34226-35-2; **26**, 34226-36-3; **27**, 34226-37-4; **28**, 34220-45-6; **29**, 34220-46-7.

Acknowledgment.—Financial support from the donors of the Petroleum Research Fund of the American Chemical Society and from the National Science Foundation is gratefully acknowledged.

---

[37] Kindly provided by Dr. E. W. Reeve, University of Maryland.

Synthetic Routes to Polyspiro Compounds with a Central Cyclobutane Ring

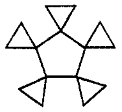
A. PAUL KRAPCHO,* D. E. HORN, D. R. RAO, AND B. ABEGAZ[1]

Department of Chemistry, University of Vermont, Burlington, Vermont 05401

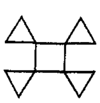
Received October 5, 1971

The reaction of dione **3** ($n = 6$) with triphenylphosphinemethylene in a benzene solution leads to **4** ($n = 6$) in 15–20% yields along with **9** ($n = 6$). On the other hand, **3** ($n = 5$) on treatment with this ylide leads only to the ring-opened product **9** ($n = 5$). Treatment of **6** with dimethylsulfoxonium methylide leads to **12**. The diepisulfides **13** and **14** ($n = 5$ or 6) undergo smooth desulfurization on heating with tri-*n*-butylphosphine to yield **7** and **4** ($n = 5$ or 6), respectively, in good yields. The dienes **7** and **4** ($n = 5$ or 6) on treatment with the Simmons-Smith reagent lead to **16** and **5** ($n = 5$ or 6). The trispirenes **15** ($n = 5$) and **17** were also isolated. The nmr data for the trispiro and tetraspiro systems along with **16** and **17** are presented and briefly discussed.

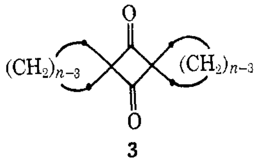
The synthesis of pentaspiro[2.0.2.0.2.0.2.0.2.0]pentadecane (**1**) has recently been described by Ripoll and Conia.[2] This was the first report of the preparation of this type of polyspiro system and the general name "rotane" was suggested because of the paddle-wheel-like arrangement of the outer cyclopropane rings. Shortly thereafter, the synthesis of tetraspiro[2.0.2.0.2.0.2.0]dodecane (**2**) was reported.[3,4]



1



2



3

We wish to report synthetic routes to "rotanes" possessing an internal four-membered ring flanked by "blades" of varying ring size. The original synthetic scheme centered on the readily available polymethyleneketene dimers **3** ($n = 5$ or 6) as potential starting materials.[5] It was envisioned that treatment

---

[1] Ethiopian Fellow of the African Graduate Fellowship Program (AFGRAD).

[2] (a) J. L. Ripoll and J. M. Conia, *Tetrahedron Lett.*, 979 (1969); (b) J. L. Ripoll, J. C. Limasset, and J. M. Conia, *Tetrahedron*, **27**, 2431 (1971).

[3] J. M. Conia and J. M. Denis, *Tetrahedron Lett.*, 3545 (1969).

[4] P. Le Perchec and J. M. Conia, *ibid.*, 1587 (1970).

[5] J. L. E. Erickson, F. E. Collins, Jr., and B. L. Owen, *J. Org. Chem.*, **31**, 480 (1966).