Synthesis of Sultones from Hexachlorobicyclo[2.2.1]heptenes and -heptadienes

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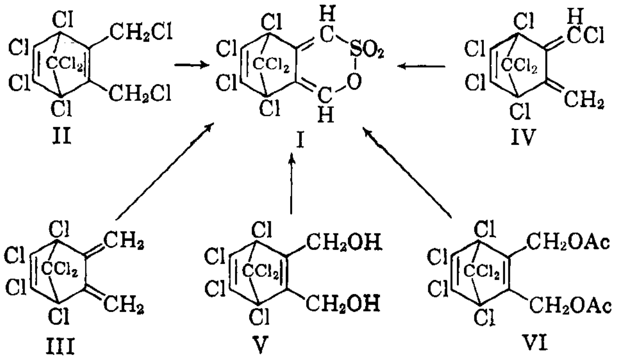
1,2,3,4,7,7-Hexachloro-5-(hydroxymethylene)-6-(sulfomethylene)bicyclo[2.2.1]hept-2-ene sultone is produced by reaction of oleum with any of the following: 2,3-bis(chloromethyl)-1,4,5,6,7,7-hexachlorobicyclo[2.2.1]-heptadiene, 5-(chloromethylene)-6-methylene-1,2,3,4,7,7-hexachlorobicyclo[2.2.1]hept-2-ene, 5,6-bis(methylene)-1,2,3,4,7,7-hexachlorobicyclo[2.2.1]hept-2-ene, 2,3-bis(hydroxymethyl)-1,4,5,6,7,7-hexachlorobicyclo[2.2.1]heptadiene, or 2,3-bis(acetoxymethyl)-1,4,5,6,7,7-hexachlorobicyclo[2.2.1]heptadiene. The reaction of oleum with 1,2,3,4,7,7-hexachlorobicyclo[2.2.1]heptadiene yields 1,2,3,4,7,7-hexachloro-3-hydroxy-5-sulfotricyclo[2.2.1.0^{2,6}]-heptane sultone. The reaction of oleum with 5-methylene-1,2,3,4,7,7-hexachlorobicyclo[2.2.1]hept-2-ene yields, *via* a skeletal rearrangement, 1,2,3,5,6,6-hexachloro-5-hydroxy-4-(sulfomethyl)bicyclo[2.2.1]hept-2-ene sultone. Spectroscopic and chemical evidence is presented for these structures.

The Diels–Alder reaction of hexachlorocyclopentadiene with 1,4-disubstituted 2-butynes has given access to a series of new 5,6-disubstituted 1,2,3,4,7,7-hexachlorobicyclo[2.2.1]hept-2-enes and -heptadienes (II–VI).[1] In the course of an investigation of the chemistry and pesticidal utility of this series, it has been found that compounds II–VI undergo reaction with fuming sulfuric acid to yield a novel dienic sultone, 1,2,3,4,7,7-hexachloro-5-(hydroxymethylene)-6-(sulfomethylene)-bicyclo[2.2.1]hept-2-ene sultone (I).

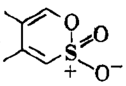


The structure of I is established by its elemental analysis, molecular weight, absence of acidic hydrogen, and spectral properties. An infrared absorption band at 6.24 μ is characteristic of the –CCl=CCl– structure as found in hexachlorobicyclo[2.2.1]heptenes.[2] Infrared bands at 6.11 and 5.93 μ indicate the presence of two other C=C bonds, probably conjugated. Bands at 7.26 (shoulder at 7.42) and 8.61 μ are found reasonably near the positions (7.44 and 8.65 μ) reported for the $-SO_2-O-$ structure in a dienic δ-sultone by Helferich, *et al.*[3] The nuclear magnetic resonance spectrum showed an AB pattern, with two close doublets (J = 1.2 c.p.s.) of equal intensity at 6.70 and 7.03 p.p.m.[4]

The reaction of oleum with 5,6-bis(methylene)-1,2,3,4,7,7-hexachlorobicyclo[2.2.1]hept-2-ene (III) to yield I involves stoichiometrically an oxidative dehydrogenation. The evolution of sulfur dioxide was noted during the reaction, indicating that the oleum was functioning as an oxidant.

Although oleum containing 20% sulfur trioxide was found to be the most satisfactory reagent (from the standpoint of yield and ease of handling) for preparing sultone I, it was found possible to prepare the same product by the reaction of liquid sulfur trioxide (commercial, stabilized sulfuric anhydride) with 2,3-bis-(chloromethyl)-1,4,5,6,7,7-hexachlorobicyclo[2.2.1]heptadiene (II).

The ready formation of the dienic δ-sultone ring system from a variety of starting materials (particularly from III by dehydrogenation) and its stability to oleum suggested the possibility of this ring system possessing a considerable degree of resonance stabilization, perhaps approaching aromatic character. Canonical resonance forms such as C–F would permit the positive charge localized on the sulfur atom in A and B to be distributed in part to the ring oxygen atom. Analogous resonance forms involving the 3d-orbitals of sulfur have been adduced to explain the conjugative effects of the *p*-methylsulfonyl group in anilines and phenols,[5a] and the stabilization of carbanions by sulfonyl groups.[5b]

A


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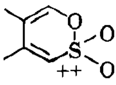
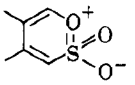


C


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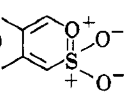

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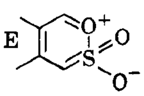

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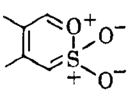

However, examination of the n.m.r. spectrum of I indicated that the diene–sultone ring system represents, at most, a borderline case of aromaticity. Regardless of which of the two observed absorption peaks is assigned to the proton adjacent to the ring oxygen in I, it is evident that this proton falls roughly midway between a typical nonaromatic cyclic vinyl ether α-hydrogen (examples: dihydropyran, δ — 6.37; 2,6-dimethyl-γ-pyrone, δ = 6.03)[6] and an aromatic vinyl ether (example: furan, δ = 7.42[6]).

Although a substantial number of dienic δ-sultones have been described,[7] no previous examples were found having a hydrogen atom rather than an alkyl group on the oxygen-substituted (δ) carbon. Only one route to dienic δ-sultones has hitherto been described, namely the cyclization of β-branched α,β- or β,γ-unsaturated

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[1] P. E. Hoch and J. M. Clegg, *J. Am. Chem. Soc.*, **81**, 5413 (1959).

[2] E. T. McBee, D. K. Smith, and H. E. Ungnade, *ibid.*, **77**, 559 (1955).

[3] B. Helferich, R. Dhein, K. Geist, H. Junger, and D. Wiehle, *Ann.*, **646**, 32 (1961).

[4] δ relative to tetramethylsilane. The spectrum was run in deuteriochloroform, by courtesy of Varian Associates Instrument Division, using a Model A-60 high resolution spectrometer.

[5] (a) C. C. Price and S. Oae, "Sulfur Bonding," Ronald Press Co., New York, N. Y., 1962, pp. 71, 123; (b) W. A. Pryor, "Mechanisms of Sulfur Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p. 33.

[6] "High Resolution N.M.R. Spectra Catalog," Varian Associates, Palo Alto, Calif., 1962, Spectra No. 111, 166, and 50.

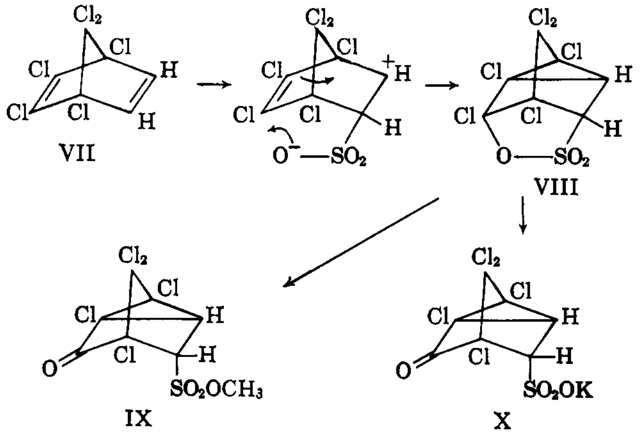
[7] W. Treibs, *Ber.*, **70**, 85 (1937); T. Morel and P. E. Verkade, *Rec. trav. chim.*, **67**, 539 (1948); **68**, 619 (1949); **70**, 35 (1951); reviewed and tabulated by A. Mustafa, *Chem. Rev.*, **54**, 195 (1954).

ketones (or corresponding ketols) by concentrated sulfuric acid in the presence of acetic anhydride. The reactions found in the present investigation, therefore, represent several new routes to the dienic δ-sultone structure.

In view of these unexpected findings concerning the reaction of oleum with 5,6-disubstituted hexachlorobicyclo[2.2.1]heptenes or -heptadienes, it was of interest to investigate the reaction of oleum with related compounds having only one side chain or lacking a side chain.

The reaction of oleum with 1,2,3,4,7,7-hexachlorobicyclo[2.2.1]heptadiene (VII)[8] yielded a nonacidic crystalline product of the empirical formula $C_7H_2Cl_6O_3S$ to which the structure VIII is assigned on the basis of the following evidence. The infrared spectrum of this compound showed no trace of absorption in the C=C region; a band appeared at 9.56 μ which coincides with the cyclopropane ring absorption reported for *trans*-1,2-dichlorocyclopropane.[9] Treatment of VIII with sodium carbonate in methanol caused release of one molar equivalent of chloride ion per mole of sultone and yielded a neutral water-insoluble crystalline product (IX) of empirical formula $C_8H_5Cl_5O_4S$; treatment of VIII with potassium hydroxide in methanol yielded one molar equivalent of chloride ion, a small amount of ester IX, and a larger amount of a salt X having the correct analysis for $C_7HCl_5O_4KS{\cdot}H_2O$. Both IX and X showed strong infrared absorption at 5.5 μ, characteristic of a transannular carbonyl bridge.[2,10]

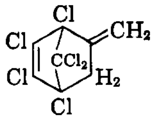
The formation of VIII may be viewed as proceeding *via* a carbonium ion in which the norbornene → norcarane rearrangement occurs.



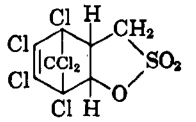
VII VIII IX X

The reaction of 5-methylene-1,2,3,4,7,7-hexachlorobicyclo[2.2.1]hept-2-ene[11] (XI) with oleum yielded a crystalline product of the empirical formula $C_8H_4Cl_6O_3S$ (XII), evidently a sultone in view of its elemental analysis, nonacidic character, and hydrolytic properties. The infrared spectrum of XII exhibited only one band in the carbon-to-carbon double bond region, at 6.21 μ, characteristic of the –CCl=CCl–group in chlorine-containing bicyclo[2.2.1]heptenes,[2] thus eliminating possible structures analogous to VIII. Hydrolysis of XII in aqueous tetrahydrofuran resulted in opening of the sultone ring with the release of one equivalent of hydrochloric acid and with the formation of a ketonic sulfonic acid, $C_8H_5Cl_5O_4S$ (XIII, isolated as the dihydrate and as the barium salt).

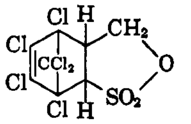
This behavior on hydrolysis eliminates structures XIIa and XIIb for the sultone $C_8H_4Cl_6O_3S$.



XI

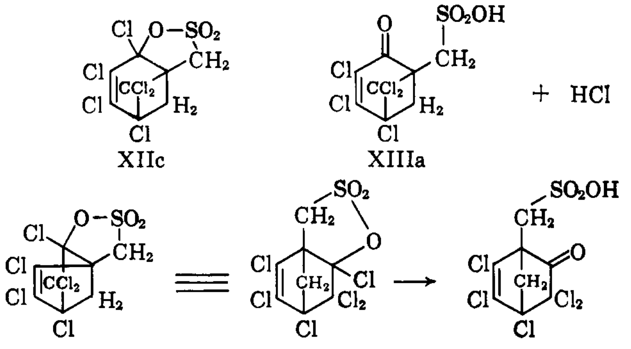


XIIa



XIIb

Two sterically feasible structures, XIIc and XIId, both of which would involve skeletal rearrangements in their formation from XI, may be hypothesized to account for the presence of the –CCl–O– group and the formation of the keto group on hydrolysis.



XIIc XIIIa XIId XIIIb

A priori, structure XIIc appeared less probable than XIId, since no examples of carbonium ion rearrangements from the bicyclo[2.2.1]hept-2-ene skeleton to the bicyclo[3.1.1]hept-2-ene skeleton were found in the literature, whereas skeletal rearrangements of the type required to form XIId have been shown to occur in the norbornene series.[12]

Both ultraviolet and infrared evidence favor structure XIIIb for the ketonic hydrolysis product and thus favor structure XIId for the sultone.[13] The ultraviolet spectrum of the ketonic hydrolysis product (as the acid) in ether shows a strong maximum at 235–240 mμ (ε ~7000)[14] comparable to $\lambda_{\max}^{\text{cyclohexane}}$ 236–237 mμ (ε 9200) reported for the unconjugated isomer of octachlorocyclohexenone.[15]

The hypothetical conjugated structure XIIIa would be expected to have $\lambda_{\max}$ of at least 267 mμ by com-

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(8) M. Kleiman (to Velsicol Chemical Corp.), U. S. Patent 2,736,730 (1956); *Chem. Abstr.*, **50**, 10,780*h* (1956).

(9) V. A. Slabey, *J. Am. Chem. Soc.*, **76**, 3604 (1954).

(10) P. Yates and P. Eaton, *Tetrahedron*, **12**, 13 (1961).

(11) W. K. Johnson and V. Mark, *J. Org. Chem.*, **26**, 4105 (1961).

(12) J. D. Roberts, C. C. Lee, and W. H. Saunders, Jr., *J. Am. Chem. Soc.*, **77**, 3034 (1955); S. Winstein and M. Shatavsky, *Chem. Ind.* (London), 56 (1956).

(13) While the possibility of a skeletal rearrangement from XIIc to XIIIb during the hydrolytic ring opening has not rigorously been excluded, it seems quite improbable that such a rearrangement would take place under the hydrolytic conditions while not occurring under the conditions of the formation of the sultone in oleum. It is possible to postulate an intermediate carbonium ion common to both the ring-forming and ring-opening reactions, such an ion possibly being a resonance hydrid of "norpinene" and "norbornene" canonical forms. However, since this ion fails to react in the "norpinene" form with water to yield the hypothetical conjugated ketone XIIIa, where the resonance stabilization of the conjugated structure would seem to favor this path, it is difficult to see why the intermediate carbonium ion should undergo sultone ring closure in the "norpinene" form where no evident energy relationship would favor such a path.

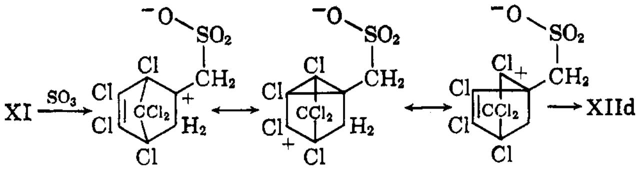
(14) It should be further noted that the ketonic hydrolysis product (XIIIb) exhibits a weak broad band at 312 mμ (ε 350) which may be attributed to the n→π* transition of the carbonyl group. This broad band is comparable to the resolved n→π* quadruplet [287 mμ (ε 162), 296.5 (242), 307.5 (277), 319.5 (177)] reported for bicyclo[2.2.1]hept-5-en-2-one by A. Moscowitz, K. Mislow, M. A. W. Glass, and C. Djerassi [*J. Am. Chem. Soc.*, **84**, 1945 (1962)].

(15) L. Denivelle and R. Fort, *Bull. soc. chim. France*, 459 (1958).

parison with the reported spectrum of the conjugated isomer of octachloro-2-cyclohexenone. The four-membered ring would in fact be expected to raise the λ_{max} of the hypothetical XIIIa, as can be seen by comparison of the spectrum of verbenone (253 mμ)[16] with that of isophorone (234 mμ).[17]

The carbonyl band of the ketonic hydrolysis product occurs at 5.60 μ, identical with the position reported for 1,2,3,4,7,7-hexachlorobicyclo[2.2.1]hept-2-en-5-one[11] and substantially identical with the position reported for the unconjugated isomer of octachlorocyclohexenone.[15] On the other hand, the carbonyl absorption of the less-favored hypothetical structure XIIIa would be expected to occur in the vicinity of 5.73, the value reported for 1,3,4,4,5,5,6,6-octachloro-2-cyclohexenone.[18] The presence of the four-membered ring in XIIIa would be expected to have little influence on the position of the carbonyl absorption, as can be seen from a comparison of verbenone, $\lambda_{C=O}$ 5.93 μ[16] to isophorone, $\lambda_{C=O}$ 5.95 μ.[17]

The formation of XIId from XI may be explained on the basis of a carbonium ion rearrangement as shown.



The redistribution of the positive charge to the former bridgehead carbon makes possible a facile ring closure to form the γ-sultone XIId.

Experimental

1,2,3,4,7,7-Hexachloro-5-(hydroxymethylene)-6-(sulfomethylene)bicyclo[2.2.1]hept-2-ene Sultone (I). A. From 2,3-Bis(chloromethyl)-1,4,5,6,7,7-hexachlorobicyclo[2.2.1]heptadiene (II).—Twenty grams of 2,3-bis(chloromethyl)-1,4,5,6,7,7-hexachlorobicyclo[2.2.1]heptadiene[1] and 50 ml. of oleum (20% sulfur trioxide) were heated at 72–76° for 30 min. with stirring. The dark homogeneous solution then was cooled and poured cautiously with stirring into ice–water. The sticky precipitate was extracted with benzene. The benzene extracts were washed with water, dried over magnesium sulfate, filtered, and evaporated to dryness to obtain 19 g. of tan solid, m.p. 127–129.5°.

Recrystallization from carbon disulfide yielded 17 g. (84%) of colorless crystals, m.p. 129–130°. The product is insoluble in water, slightly soluble in cold heptane, moderately soluble in hot heptane, and soluble in cold benzene; λ_{max}^{Nujol} 3.27 (w), 5.93 (m), 6.11 (w), 6.24 (m), 7.26 (s, only partly due to Nujol), 7.42 (shoulder), 7.97 (w), 8.32 (s), 8.50 (w), 8.61 (m), 8.86 (shoulder), 8.93 (s), 9.11 (w), 9.62 (w), 9.80 (m), 10.34 (w), 10.89 (m), 11.51 (m), 11.83 (m), 12.10 (m), 12.53 (w), 12.86 (m), 14.50 (s), 14.65 (s), and 15.11 μ (m). The compound is neutral to congo red indicator in aqueous ethanolic solution.

Anal. Calcd. for $C_9H_2Cl_6SO_3$: C, 26.80; H, 0.50; Cl, 52.9; S, 7.94; mol. wt., 405. Found: C, 26.84; H, 0.55; Cl, 52.8; S, 7.99; mol. wt., 388 (± 10%, ebullioscopic in benzene).

In a modification of the above procedure, 20 g. of 2,3-bis(chloromethyl)-1,4,5,6,7,7-hexachlorobicyclo[2.2.1]heptadiene was added in portions to 50 ml. of liquid sulfur trioxide (Stabilized Sulfan, Allied Chemical Corp.), maintaining the temperature below 50°. After 10 min., the reaction mixture was worked up as above to obtain 6.4 g. (32%) of I.

B. From 5-(Chloromethylene)-6-methylene-1,2,3,4,7,7-hexachlorobicyclo[2.2.1]hept-2-ene (IV).—Five grams of 5-(chloromethylene)-6-methylene-1,2,3,4,7,7-hexachlorobicyclo[2.2.1]-hept-2-ene[1] was added with stirring to 12.5 ml. of oleum (20% sulfur trioxide). The organic liquid quickly dissolved and the temperature rose to about 40°. In 15 min., the reaction mixture set to a semisolid dark sludge. It then was heated to 80° over a period of 30 min., then cooled, and added to ice–water; the organic precipitate was extracted with chloroform, and the chloroform was evaporated. The residual solid was recrystallized from hot heptane to obtain 5 g. of crystalline product, m.p. 129.5–131°, which was shown by infrared and mixture melting point to be identical with the product of method A.

C. From 5,6-Bis(methylene)-1,2,3,4,7,7-hexachlorobicyclo-[2.2.1]hept-2-ene (III).—To 50 ml. of oleum (20% sulfur trioxide) was added 10 g. of 5,6-bis(methylene)-1,2,3,4,7,7-hexachlorobicyclo[2.2.1]hept-2-ene.[1] An exotherm to about 40° resulted, the characteristic odor of sulfur dioxide became evident, and within 30 min. the organic solid had almost completely dissolved. The dark solution was filtered through a sintered-glass funnel and then cautiously added to ice–water with stirring. The resultant gummy precipitate was taken up in benzene, washed with water, and evaporated to dryness. The yellowish residual solid (which appeared to be contaminated with sulfur), after three recrystallizations from heptane, yielded 4 g. of colorless needles melting at 128–129°. The identity of this product with that of method A was established by mixture melting point and infrared spectrum.

D. From 2,3-Bis(hydroxymethyl)-1,4,5,6,7,7-hexachlorobicyclo[2.2.1]heptadiene (V).—To 50 ml. of oleum (20% sulfur trioxide) was added 10 g. of 2,3-bis(hydroxymethyl)-1,4,5,6,7,7-hexachlorobicyclo[2.2.1]heptadiene,[1] with stirring. The solution rapidly darkened as the solid was added, and the temperature rose to 50°. After several hours, the solution was poured cautiously into ice–water, the resultant milky suspension was extracted with chloroform, and the chloroform extract was washed with water. Upon stripping the chloroform, a semisolid mass was obtained. This product was treated in warm heptane with Fuller's earth and charcoal, isolated by chilling, and recrystallized again from heptane to obtain colorless crystals, m.p. 129.5–130.5°. The infrared spectrum and mixture melting point established this product to be identical with the product of method A.

E. From 2,3-Bis(acetoxymethyl)-1,4,5,6,7,7-hexachlorobicyclo[2.2.1]heptadiene[1] (VI).—Two grams of the diacetate[1] and 5 ml. of oleum (20% sulfur trioxide) were heated on the steam bath 3 hr., cooled, and poured into ice–water; the organic product was extracted with chloroform and the chloroform washed with water. Upon evaporation of the chloroform, an oil remained which crystallized on standing. This was taken up in hot heptane, and on chilling the solution deposited 1.5 g. of crystals, m.p. 112–119°. The infrared spectrum of this product showed that it consisted of a mixture of the sultone (I) with about an equal amount of one or more contaminants exhibiting an -OH group (2.92 μ) and a carbonyl group (5.76 μ).

1,2,3,4,7,7-Hexachloro-3-hydroxy-5-sulfotricyclo[2.2.1.0^{2,6}]heptane Sultone (VIII).—Ten grams of 1,2,3,4,7,7-hexachlorobicyclo[2.2.1]heptadiene (VII)[8] and 20 ml. of oleum (20% sulfur trioxide) were stirred and heated, the temperature being raised to 80° over 15 min. The reaction mixture partially solidified. It was cooled and added to ice–water; the precipitated solids were removed by filtration and washed with water. The crude product was dissolved in warm heptane; the solution was filtered with Fuller's earth and charcoal, and chilled to obtain 6 g. of colorless needles, m.p. 173.5–174°; λ_{max}^{Nujol} 7.50 (w), 8.07 (s), 8.30 (m), 8.60 (m), 8.80 (w), 9.05 (s), 9.11 (s), 9.56 (m), 10.17 (m), 10.27 (s), 10.71 (m), 11.44 (m), 11.87 (s), 12.16 (s), 12.6 (m), 13.26 (vs), 14.13 (m), and 15.00 μ (m). The compound is neutral to congo red indicator in aqueous ethanolic solution.

Anal. Calcd. for $C_7H_2Cl_6O_3S$: C, 22.19; H, 0.53; Cl, 56.15; S, 8.46; mol. wt., 379. Found: C, 22.29; H, 0.66; Cl, 56.4; S, 8.46; mol. wt., 357 (± 10%, ebullioscopic in tetrahydrofuran).

Methyl 1,2,4,7,7-Pentachloro-3-ketotricyclo[2.2.1.0^{2,6}]heptane-5-sulfonate (IX).—A mixture of 10 g. of the sultone (VIII), 6 g. of anhydrous sodium carbonate, and 75 ml. of methanol was agitated for 10 min. with water-bath cooling. The mixture became thicker as solids came out of solution. The solids were removed by filtration and washed with water to remove inorganic salts. Volhard titration of the methanol filtrate and water washings showed 19.7 mequiv. of chloride to be present (theory, 26.4 mequiv.).

The water-insoluble solids were dried quickly *in vacuo* and recrystallized twice from benzene–heptane mixture to obtain 3 g.

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(16) C. H. Whitham, University of Birmingham, private communication.

(17) R. L. Erskine and E. S. Waight, *J. Chem. Soc.*, 3425 (1960).

(18) L. Denivelle and R. Fort, *Bull. soc. chim. France*, 392 (1959).

of colorless needles, m.p. 171–171.5°; λ_{max}^{Nujol} 5.40 (s), 7.37 (s), 8.14 (w), 8.46 (s), 9.53 (mw), 10.17 (s), 10.34 (w), 11.08 (w), 11.39 (m), 11.70 (w), 12.16 (m), 12.64 (m), 13.07 (m), and 13.66 μ (w).

Anal. Calcd. for $C_8H_7Cl_5O_4S$: C, 25.5; H, 1.86; Cl, 47.2; S, 8.50. Found: C, 25.8; H, 1.81; Cl, 47.2; S, 8.43.

Potassium 1,2,4,7,7-Pentachloro-3-ketotricyclo[2.2.1.0^{2,6}]heptane-5-sulfonate (X).—By employing potassium hydroxide in place of sodium carbonate in the above reaction, 1.2–1.3 equiv. of chloride ion per mole was released. The methyl ester (IX) was obtained in varying but minor amounts, the principal products being methanol-soluble salts. From the methanol filtrate on successive partial evaporations, a series of three water-soluble crystalline crops were obtained which, on the basis of infrared spectra, were primarily the same compound. The first and last crops contained a tenacious unsaturated impurity (band at 6.1 μ), but the second crop was substantially free of carbon-to-carbon double bond absorption. All crops showed strong C═O absorption at 5.52 μ. The second crop was used for elemental analysis.

Anal. Calcd. for $C_7HCl_5O_4KS \cdot H_2O$: C, 20.23; H, 0.73; Cl, 42.7; S, 7.72. Found: C, 20.46; H, 1.03; Cl, 41.5; S, 7.72.

1,2,3,5,6,6-Hexachloro-5-hydroxy-4-(sulfomethyl)bicyclo[2.2.1]hept-2-ene Sultone (XII).—To 300 ml. of oleum (20% sulfur trioxide) was added 100 g. of 5-methylene-1,2,3,4,7,7-hexachlorobicyclo[2.2.1]hept-2-ene[11] with stirring and water-bath cooling to hold the temperature below 50°. After the mixture had been stirred for 30 min., during which time it became a thick crystal slurry, it was added to ice–water. The precipitated solid was extracted with methylene chloride, washed with water, dried over magnesium sulfate, and filtered, and about an equal amount of carbon tetrachloride was added. Partial evaporation yielded 83 g. of crystalline solid, m.p. 185–187.5°.

Recrystallization from methylene chloride–carbon tetrachloride yielded colorless needles, m.p. 192.5°; λ_{max}^{Nujol} 3.31 (w), 6.21 (m), 7.00 (w), 7.20 (s, partly Nujol), 7.59 (w), 7.94 (m), 8.12 (m), 8.24 (m), 8.48 (s), 8.80 (w), 8.97 (w), 9.27 (m), 9.43 (s), 9.54 (s), 9.83 (w), 9.98 (w), 10.35 (m), 10.76 (ms), 11.2 (sh), 11.33 (s), 11.77 (m), 12.28 (m), 12.51 (m), 13.20 (m), 14.12 (m), 14.82 (w), and 15.22 μ (w). The compound is neutral to congo red in aqueous ethanolic solution.

Anal. Calcd. for $C_8H_4Cl_6O_3S$: C, 24.35; H, 1.27; Cl, 54.0; S, 8.11; mol. wt., 393. Found: C, 24.35; H, 1.36; Cl, 54.1; S, 7.98; mol. wt., 423 (± 10%; ebullioscopic in benzene).

1,2,3,6,6-Pentachloro-4-(sulfomethyl)bicyclo[2.2.1]hept-2-en-5-one (XIII) and Barium Salt.—A solution of 3.93 g. (10 mmoles) of the sultone XII in 90 ml. of tetrahydrofuran and 10 ml. of water was refluxed for 27 hr. An aliquot was found to contain 7.3 mequiv. of chloride by Volhard titration. A blank experiment wherein 1 *N* hydrochloric acid in 1:9 water–tetrahydrofuran solution was refluxed for a similar period showed that one-quarter of the hydrochloric acid was consumed by reaction with the tetrahydrofuran; therefore, taking into consideration this loss of hydrogen chloride, approximately 1 equiv. of hydrogen chloride per mole of XII had been evolved. Potentiometric titration of a second aliquot with 0.1 *N* sodium hydroxide gave an unsharp end point in the vicinity of pH 5 (the fading end point attributable to the instability of XIII sodium salt toward aqueous base) indicating the formation of 2 equiv. of strong acid per mole of XII.

The reaction mixture was evaporated to obtain a gray solid, m.p. 159.5–164°, which was recrystallized from benzene–ether and dried in air to obtain 2 g. of grayish white crystals, m.p. 163–165°; λ_{max}^{Nujol} 5.61 (C═O) and 6.28 μ (C═C); λ_{max}^{ether} 235 mμ (ε ~7000, on side of intense band < 220 mμ), 312 mμ (ε 350). The compound is soluble in water, giving a solution acidic to congo red indicator.

Anal. Calcd. for $C_8H_5Cl_5O_4S \cdot 2H_2O$: C, 23.41; H, 2.21; Cl, 43.19; S, 7.81. Found: C, 23.76; H, 2.41; Cl, 43.3; S, 8.20.

To obtain a more precise analysis, XIII was converted to its barium salt by digesting it in aqueous solution with an equimolar amount of barium carbonate on the steam bath until effervescence ceased (2.5 hr.), the mixture was filtered while hot, the filtrate was concentrated and cooled, and the resultant precipitate was filtered out and dried in air to obtain tan nodular crystals, λ_{max}^{Nujol} 5.60 (C═O) and 6.26 μ (C═C).

Anal. Calcd. for $C_{16}H_8BaCl_{10}O_8S_2 \cdot H_2O$: C, 21.29; H, 1.12; Ba, 15.2; Cl, 39.31; H_2O, 1.99; S, 7.10. Found: C, 21.09; H, 1.17; Ba, 14.9; Cl, 39.30; H_2O, 1.86; S, 7.02.

The Addition of Dichlorocarbene to *cis,cis*-1,5-Cyclooctadiene

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The reaction cited in the title can be conducted very smoothly by refluxing the hydrocarbon in a suspension of sodium trichloroacetate in a mixture of tetrachloroethylene and a small amount of diethylene glycol dimethyl ether. The reaction affords two crystalline bis adducts, and X-ray analysis has shown that the major, lower melting product has the *cis* configuration.

The objective of this investigation was to develop a carbene reaction suitable for use as an experiment for beginning students. The starting materials should be readily available, the reaction time short, and the product an easily isolated solid. The reaction of tetrachloroethylene with dichlorocarbene to give hexachlorocyclopropane (m.p. 104°) meets the requirements only in part. The yield is satisfactory (74%) when the intermediate is generated from phenyl(bromodichloromethyl)mercury,[2] but the preparation of this reagent is too involved and expensive. The double bond of tetrachloroethylene is so inert that generation of dichlorocarbene from chloroform or from sodium trichloroacetate in the presence of this olefin affords hexachlorocyclopropane in yields of 0.2–10%.[3,4]

It seemed to us that the bis adduct of a nonconjugated diene should have favorable properties and that *cis,cis*-1,5-cyclooctadiene offered particular promise. The hydrocarbon is available commercially[5] and has been found to react readily with hexachlorocyclopentadiene at 100° to give a high melting bis adduct.[6] Indeed, Skatteböl[7] states in a preliminary report that the cyclodiene reacts with dibromocarbene generated from bromoform and potassium *t*-butoxide to give a liquid mono adduct and a bis adduct melting at 174–180°. Since the completion of our work, Fray[8] has reported that reaction of the diene with sodium tri-

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