gated further. The total yield of crystalline *cis*-3,3-diphenylcyclopropane-1,2-dicarboxylic acid from ozonolysis of the photoketone was 77.5 mg. (56.5% of theory). This establishes that the photoketone must be 6,6-bicyclo[3.1.0] hex-3-en-2-one.

Ozonolysis Run II.—The ozonolysis procedure above was repeated as exactly as possible on a sample of 77 mg. of the phototoketone. The acidic residue was 76 mg. from which 26 mg. of *cis*-3,3-diphenylcyclopropane-1,2-dicarboxylic acid, m.p. 168–174° dec. could be obtained. Again, the acid had an infrared spectrum identical with that of the authentic diacid. The diacid was converted to the corresponding diester, 5.8 mg., m.p. 69–73°, which also had an infrared spectrum identical with that of the authentic diester.

Hydrogenation of the Photoketone (6,6-Diphenylbicyclo-[3.1.0]-hex-3-en-2-one).—The photoketone was hydrogenated using a standard micro hydrogenation apparatus, employing 5.9 mg. of the ketone in 8 ml. of ethanol containing 17 mg. of 10% palladium-on-charcoal catalyst at 21.8° and 738.2 mm. Hydrogen uptake was rapid as 1.125 ml. was absorbed in 10 min. and 1.270 ml. after 3.5 hr. One equivalent of hydrogen, under these conditions, was 0.639 ml.; thus, 2.0 equivalents of hydrogen was absorbed. Separation of the catalyst and evaporation of the solvent left 4 mg. of a residue whose infrared spectrum possessed an intense carbonyl band at 5.70 μ (1755 cm.$^{-1}$), characteristic of a cyclopentanone.

Photolysis of Bicyclo[3.1.0]hex-3-en-2-one (Photoketone).—In the customary photolysis solvent used in the photolysis of 4,4-diphenylcyclohexadienone, 550 ml. of spectroquality dioxane and 200 ml. of water was dissolved 120 mg. of the photoketone. The solution was photolyzed for 2.0 hr. exactly as described above in the dienone photolyses, using the same potassium acid phthalate filter solution. The mixture after photolysis was concentrated until turbid, extracted three times with ether, dried over sodium sulfate and concentrated *in vacuo* to give 170 mg. of residue. This material was dissolved in ether and extracted with three 30-ml. portions of 3% sodium hydroxide. The ethereal solution was dried over sodium sulfate and concentrated to give 80 mg. of a "neutral fraction" described below. The base extracts were acidified with 10% sulfuric acid and the cloudy solution was extracted with ether. The ethereal solution was dried and concentrated leaving 56 mg. of a residue whose infrared spectrum was virtually the same as that of the photoacid obtained from photolysis of 4,4-diphenylcyclohexadienone (see above).

The "neutral" fraction obtained above had an infrared spectrum with a sharp hydroxyl band at 2.80 μ and a sharp band at 11.15 μ, both strongly indicative of the presence of 2,3-diphenylphenol. There were also two carbonyl bands at 5.65 and 5.8 μ. Attempts to obtain crystalline material from this mixture in hexane–chloroform were completely unsuccessful. A 68-mg. portion of the mixture was subjected to liquid–liquid partition chromatography as described above for the neutral fraction from the dienone photolysis. Passage through a column 3.5 × 30 cm. with ultraviolet scanning resulted in the elution of a symmetrical peak and processing gave a residue of 55 mg. This material was not pure, according to infrared analysis, as the spectrum contained a strong carbonyl band at 5.80 μ and a few other weaker bands in addition to all the bands present in the spectrum of 2,3-diphenylphenol. A second passage through a column 3.5 × 100 cm. again led to the elution of material which gave a symmetrical peak, but whose infrared spectrum was unchanged from that of the material put on the column. It was suspected from earlier work that small traces of impurities, suspected to be benzoate esters, in the dimethylformamide used in the chromatography were contaminating the phenolic product. Therefore this residue, 46 mg., was chromatographed on a 2 × 30 cm. silica gel column. After elution of trace quantities of material with 250 ml. of hexane and 250 ml. of 5% ether–hexane, 9.7 mg. of a carbonyl compound was eluted with the next 125 ml. of 5% ether–hexane. This material contained no phenol and possessed the infrared spectrum of the solvent impurity. Fraction 5, 5.9 mg., eluted with 125 ml. of 5% ether–hexane was a mixture of the carbonyl component and the phenol while fractions 6–8, totaling 18.7 mg., eluted with 250 ml. of 10% ether–hexane and 125 ml. of 20% ether–hexane, were pure phenol. The infrared spectra of fractions 6–8 were identical with that of 2,3-diphenylphenol obtained earlier from several different sources. Fractions 6–8 were taken up in chloroform hexane and the solution was concentrated and more hexane added until the volume of the solution was about 0.3 ml. The solution was cooled and crystallization took place. The solid was separated and dried. It weighed 10.0 mg., m.p. 101.5–103.5° (2,3-diphenylphenol obtained above had m.p. 101.5–102.0°). The infrared spectrum of the solid was superimposable on that of 2,3-diphenylphenol obtained earlier.

Acknowledgment.—The authors express their appreciation to the National Science Foundation for support of this research. Similarly, appreciation is expressed to the NSF for funds (G19108) for purchase of an A60 n.m.r. instrument.

[Contribution from the Department of Chemistry, Purdue University, Lafayette, Ind.]

Nucleophilic Displacement Reactions of Hexachlorocyclopentadiene. II.[1,2] Reactions with Secondary Amines[3]

By E. T. McBee, J. O. Stoffer and H. P. Braendlin

Received April 11, 1962

In a continued study of reactions undergone by hexachlorocyclopentadiene with nucleophiles, the halide was treated with secondary aliphatic amines to give 5,5-diamino-1,2,3,4-tetrachlorocyclopentadienes. Allyl alcohol reacted with 5,5-dimorpholinyl-1,2,3,4-tetrachlorocyclopentadiene to give 5,7-methyleneoxy-7-morpholinyl-1,2,3,4-tetrachlorobicyclo[2.2.1]-hept-2-ene, an intramolecular Diels–Alder adduct, which on hydrolysis produced *exo*-5-hydroxymethyl-1,2,3,4-tetrachlorobicyclo[2.2.1]hept-2-en-7-one.

Hexachlorocyclopentadiene (I) reacts with alcoholic or thiolic bases to yield ketals[4] (II) or thioketals[5] of 2,3,4,5-tetrachlorocyclopentadienone. This remarkable reactivity of I and octachlorocyclopentene (III), the latter producing ketals of the type IV in alcoholic base, and of derivatives of the two unsaturates, was discussed more fully in the first paper of this series.[1] As a continuation of this line of study, reaction of I and III with amines deserved attention.

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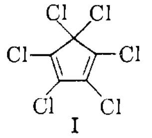
[1] For the first paper in this series see E. T. McBee, D. L. Crain, R. D. Crain, L. R. Belohlav and H. P. Braendlin, *J. Am. Chem. Soc.*, **84**, 3557 (1962).

[2] E. T. McBee, R. D. Crain, D. L. Crain, J. O. Stoffer, L. R. Belohlav and H. P. Braendlin, Abstracts of Papers, 137th Meeting, Am. Chem. Soc., Cleveland, O., April, 1960, p. 31-O.

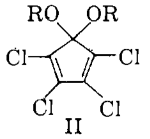
[3] This paper is based on parts of a thesis submitted by James O. Stoffer to the Graduate School of Purdue University, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[4] (a) J. A. Krynitsky and R. W. Bost, *J. Am. Chem. Soc.*, **69**, 1918 (1947); (b) J. S. Newcomer and E. T. McBee, *ibid.*, **71**, 946, 952 (1949); (c) J. W. Dawson and W. J. Croxall, U. S. Patent 2,562,893 (1952); *C. A.*, **46**, 1587 (1952).

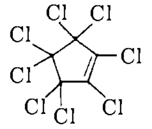
[5] E. P. Ordas, U. S. Patent 2,697,103 (1954); *C. A.*, **49**, 15956 (1955).



I



II



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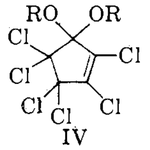
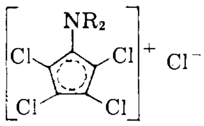
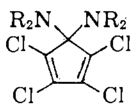


IV

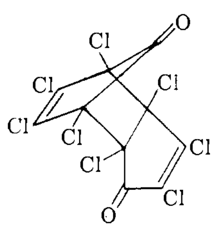
Reactions of I with secondary aliphatic amines in methanol gave 5,5-diamino-1,2,3,4-tetrachlorocyclopentadienes (VI) in good yields. Hydrolysis of VI gave the known[6] diketone VII; like most substituted cyclopentadienones,[7] tetrachlorocyclopentadienone is isolated only in this dimeric form. The *endo* configuration of VII was recently ascertained by ultraviolet-induced fusion to the cage compound VIII.[8] These displacement reactions I→VI resemble the conversions I→II. The ketals II, which can be alternately named 5,5-dialkoxytetrachlorocyclopentadienes, also hydrolyze to VII in structural evidence of the 5,5-disubstitution formulations.[9] The analogy is further stressed by the fact that no monosubstitution products are formed as intermediates. As suggested for the bimolecular alkoxide ion attack,[1] it may be reasoned that any intermediate of the formula cyclo-$C_5Cl_5NR_2$ is subject to fast displacements of allylic chlorine *via* a carbonium ion, V, in which the amino group provides additional resonance stabilization.



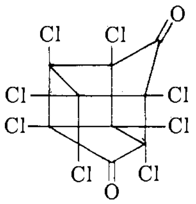
V



VI



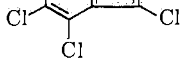
VII



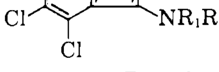
VIII

VI, R_2 = a, morpholinyl
b, piperidinyl
c, dimethyl

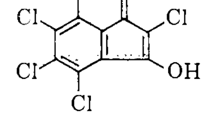
In a first attempt at obtaining VIc, chromatography on acid-washed alumina of the reaction mixture between I and dimethylamine resulted in an exothermic reaction with gas evolution, and in the isolation of IX and 3-dimethylaminopentachloroindenone (Xa). Since VII is known to convert to IX in dilute acetone,[10] by eliminating phosgene or carbon monoxide and chlorine, it is believed that VIc formed but decomposed on the column to VII, which in turn produced IX for further reaction to Xa. Compound IX was shown independently to give Xa with dimethylamine; similarly, reaction between IX and aniline is known to give Xb.[11]



IX



Xa, $R_1 = R_2 = Me$
b, $R_1 = Ph$, $R_2 = H$



XI

Another product, isolated in a small amount, from the reaction with dimethylamine was 3-dimethylamino-2,4,4,5,5-pentachloro-2-cyclopentenone (XIII). The origin of this material was ascribed to the reaction of the base with the known[12] hexachloro-2-cyclopentenone (XII), believed to be an impurity in I. The ketone XIII was prepared independently from XII and dimethylamine.

No reaction occurred between I and an aromatic secondary amine, diphenylamine. When triethylamine was added as a hydrogen chloride acceptor, diphenylamine was recovered unchanged, but a good yield of triethylamine hydrochloride was obtained. In addition, much carbon was produced as a result of decomposition of I.[13] The monounsaturate III, in contrast to its reactivity in alcoholic base, did not react with secondary amines under the conditions employed.

Attempted Diels–Alder reactions between VI and dienes or dienophiles were unsuccessful, even in the presence of base. When the latter was absent, decomposition occurred in refluxing benzene.[14] An unusual reaction took place between VIa and allyl alcohol in benzene, in the absence of morpholine. After 4 weeks at room temperature, a compound of the general formula C_{12}-

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(6) T. Zincke and K. H. Meyer, *Ann.*, **367**, 1 (1909).

(7) (a) J. Thiele, *Chem. Ber.*, **33**, 669 (1900); (b) W. von E. Doering and C. H. Depuy, *J. Am. Chem. Soc.*, **75**, 5995 (1953); (c) C. H. Depuy and D. W. Ponders, *ibid.*, **81**, 4629 (1959).

(8) P. Eaton, Ph.D. Thesis, Harvard University, 1961.

(9) With the dimorpholinyl (IIa) and dipiperidinyl (IIb) derivatives, two crystalline forms were obtained with identical infrared spectra. The higher melting (decomposition) forms resulted from recrystallizations in the presence of base and reverted to the lower melting (decomposition) forms on continued recrystallization in the absence of base. These different forms may arise from allotropy or dimorphism of the species, or from an inherent instability in the absence of extra base.

(10) P. Eaton, E. Carlson, P. Lombardo and P. Yates, *J. Org. Chem.*, **25**, 1225 (1960).

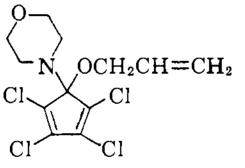
(11) T. Zincke and H. Gunther, *Ann.*, **272**, 243 (1893).

(12) E. B. Towne and H. M. Hill, U. S. Patent 2,588,997 (1952); *C. A.*, **46**, 4728 (1952).

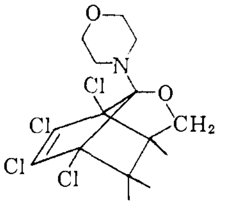
(13) This suggested the intermediate formation of a quaternary salt; such a reaction was reported between triethylamine and hexafluorocyclobutene [K. E. Rapp, *J. Am. Chem. Soc.*, **73**, 5901 (1951)]. However, reaction of I and triethylamine at room temperature resulted in complete decomposition; the only product isolated was triethylamine hydrochloride. Pyridine and I did not react in refluxing ether, but complete decomposition was observed at higher temperatures.

(14) In the reaction between VIa and maleic anhydride, in the presence of morpholine, VIa was recovered unchanged and a maleic acid morpholinide was isolated.

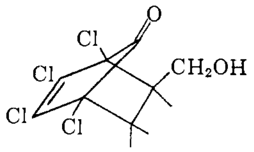
$H_{13}O_2NCl_4$ was obtained, indicating displacement of one morpholinyl group by an allyl alcohol group. It seemed likely, on the basis of microanalysis and molecular weight determination, that this product was 5-allylalkoxy-5-morpholinyl-1,2,3,4-tetrachlorocyclopentadiene (XIV). However, examination of the infrared spectrum showed only one band at 6.24 μ, indicating the presence of only one double bond. Compound VIa showed two bands, at 6.20 and 6.35 μ. The ultraviolet spectrum of the product showed the characteristic absorption of a cyclopentene; $\lambda_{\max}^{\text{EtOH}}$ 213 mμ, log ϵ 3.64. For comparison, octachlorocyclopentene has $\lambda_{\max}^{\text{EtOH}}$ 228 mμ, log ϵ 3.47.[15] The only reasonable structure in agreement with these observations is 5,7-methyleneoxy-7-morpholinyl-1,2,-3,4-tetrachlorobicyclo[2.2.1]hept-2-ene (XV). Hydrolysis of this material in acetone containing hydrochloric acid gave a quantitative yield of a compound of the general formula $C_8H_6O_2Cl_4$, to which the structure *exo*-5-hydroxymethyl-1,2,3,4-tetrachlorobicyclo[2.2.1]hept-2-en-7-one (XVI) was assigned. The placing of the hydroxymethyl group in the *exo* position resulted from the geometry of XV, assuming that no rearrangement took place during hydrolysis. Support for this assumption can be obtained by examination of the infrared spectrum of XVI: in chloroform, bands at 2.80(m), 3.00(w) and 4.45(m) μ were observed; however, in a Nujol mull the bands at 2.80 and 5.45 μ were missing, although an intense band at 3.04 μ was retained. This disappearance of the C=O and one C—OH absorption band is explained by intramolecular hemiketalization (XVII) of the hydroxyketone XVI. In the polar solvent, XVI is in equilibrium with XVII, whereas in a mull the latter is the predominant form. The band at 5.45 μ in XVI, characteristic of the bridge carbonyl group of the polychlorobicyclo[2.2.1]hept-2-en-7-one system,[16] eliminates the possibility of 1,2-addition of allyl alcohol to the cyclopentadiene. If 1,2-addition had occurred, the product from hydrolysis of XV would have a conjugated carbonyl group with an infrared absorption band at 5.75 μ.[16,17] The demonstrated reluctance of compounds of the type VI to undergo Diels–Alder addition suggests that XIV, though not isolated, indeed is a precursor to XV and readily converts to the latter by an intramolecular Diels–Alder reaction.



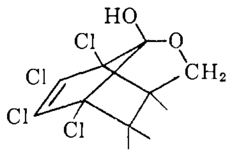
XIV



XV



XVI



XVII

Acknowledgments.—The financial assistance of the Hooker Chemical Corporation, The Standard Oil Company of Indiana and the Lubrizol Corporation is gratefully acknowledged.

Experimental[18]

5,5-Dimorpholinyl-1,2,3,4-tetrachlorocyclopentadiene (VIa).—Morpholine (34.8 g., 0.4 mole) was slowly added to hexachlorocyclopentadiene (I) (27.3 g., 0.1 mole) in 100 ml. of methanol at 0°. The mixture turned red immediately and crystals started forming after several hours. After 2 days, the product was filtered and recrystallized from ether to give 35 g. (94%) of colorless crystals, m.p. 118° dec.

Anal. Calcd. for $C_{13}H_{16}O_2N_2Cl_4$: C, 41.70; H, 4.28; Cl, 38.00; N, 7.49. Found: C, 41.40; H, 4.23; Cl, 38.08; N, 7.64.

Recrystallization from ether containing some morpholine gave 92% of colorless crystals, m.p. 135° dec.

Anal. Found: C, 41.45; H, 4.40; Cl, 38.00; N, 7.63.

The infrared spectra of the two forms, m.p. 118° and 135°, were identical both in 10% carbon tetrachloride solution and in a Nujol mull. With progressive recrystallization of VIa, m.p. 135°, from ether in the absence of morpholine, the following decreasing decomposition points were observed: 129°, 128°, 122°, 118°, 119°, 119°.

Acid Hydrolysis of VIa.—After slow addition of VIa (m.p. 118°, 12.0 g., 0.032 mole) to 200 ml. of 50% aqueous sulfuric acid, the solution was stirred and heated for 6 hr. Then 200 ml. of water was added, and the aqueous mixture extracted with ether. The ether was removed and the residue recrystallized from hexane after decolorizing with Darco. A total of 5.1 g. (73%) of VII was obtained, m.p. 165°. The mixed melting point with an authentic sample showed no depression. Also, the infrared spectrum was identical to that of a known sample.

A mixture of VIa (m.p. 135°, 5 g., 0.013 mole) and 100 ml. of 50% aqueous sulfuric acid produced, after 1 day, a solid that was filtered and recrystallized from hexane to give 2.5 g. (83%) of VII. The mixed melting point with an authentic sample gave no depression.

5,5-Dipiperidinyl-1,2,3,4-tetrachlorocyclopentadiene (VIb).—Piperidine (34.0 g., 0.4 mole) was added to I (27.3 g., 0.1 mole) in 100 ml. of methanol at 0°. The solution became red at first and within several hours crystals started forming. After 1 day, the solid was filtered and washed with methanol. Recrystallization from ether gave 34 g. (92%) of colorless crystals, m.p. 108° dec.

Anal. Calcd. for $C_{15}H_{20}N_2Cl_4$: C, 48.65; H, 5.41; Cl, 38.38; N, 7.58. Found: C, 48.68; H, 5.72; Cl, 36.49; N, 7.63.

Recrystallization from ether containing some piperidine gave 89% of colorless crystals, m.p. 116° dec.

Anal. Found: C, 48.48; H, 5.41; Cl, 38.20; N, 7.58.

The infrared spectra of the two forms were identical in both a 10% carbon tetrachloride solution and a Nujol mull.

Acid Hydrolysis of VIb. After slow addition of VIb (m.p. 108°, 5.0 g., 0.0135 mole) to 100 ml. of 25% aqueous sulfuric acid, the solution was stirred several times over a period of 2 days. The solid was filtered and the filtrate poured onto crushed ice. The crystals were dissolved in ether and the other solution was washed with water and dried over Drierite. The sulfuric acid solution was extracted with ether, but on evaporation of this solution no material was obtained. The first ether solution was concentrated and the residue recrystallized and decolorized in hexane to give 2 g. (65%) of VII. The mixed melting point with an authentic sample showed no depression.

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[15] J. D. Idol, Jr., C. W. Roberts and E. T. McBee, *J. Org. Chem.*, **20**, 1743 (1955), report $\lambda_{\max}^{\text{EtOH}}$ 230 mμ.

[16] E. T. McBee, D. K. Smith and H. E. Ungnade, *J. Am. Chem. Soc.*, **77**, 559 (1955).

[17] P. Yates and P. Eaton, *Tetrahedron*, **12**, 13 (1961).

[18] Analyses were performed by Dr. C. S. Yeh, Purdue University. The infrared spectra were determined by Miss Marjory Haley and Mrs. Wendell Dilling, Purdue University, using a Perkin-Elmer recording infrared spectrophotometer, model 21. Ultraviolet spectra were determined using a Cary recording spectrophotometer. All melting points and boiling points are uncorrected.

A sample of VIb, m.p. 116°, hydrolyzed in the same manner and 65% of VII was obtained.

Reaction of I with Dimethylamine.—Dimethylamine hydrochloride (32.6 g., 0.4 mole) and I (27.3 g., 0.1 mole) were mixed in 200 ml. of methanol. The flask was cooled in a salt–ice-bath at −10° and potassium hydroxide (22.4 g., 0.4 mole) in 200 ml. of methanol was slowly added over a period of 2 hr. After 1 day, the potassium chloride was filtered and the methanol removed under reduced pressure. Water (100 ml.) and ether (100 ml.) were added to the residue and the mixture was shaken. After separation and washing of the ether solution with water, it was dried over Drierite. Evaporation of the ether gave a brown liquid to which hexane was added. On cooling, crystals separated which were filtered, recrystallized and decolorized with Darco from hexane to give 0.9 g. (2.7%) of colorless needles, m.p. 118–119°, $\lambda_{\max}^{\mathrm{CHCl_3}}$ 5.80 μ. The mixed melting point with an authentic sample of XIII showed no depression.

Anal. Calcd. for $C_7H_6ONCl_5$: C, 28.24; H, 2.02; Cl, 59.66; N, 4.74. Found: C, 28.32; H, 2.20; Cl, 60.25; N, 4.82.

Removal of the hexane from the filtrate gave a brown oil which was dissolved in 20 ml. of hexane and chromatographed on a 20 mm. × 25 cm. column packed with acid-washed aluminum oxide. Hexane was used as the eluent. The column, on first contact with the materials, became very hot and a gas was given off. This caused severe channeling and separation in the column. After the exothermic reaction subsided, the separation was continued. The first two fractions contained 14.9 g. (54% recovery) of I. On removal of the solvent, fractions 3 through 11 gave a red oil which, on treatment with hexane and decolorization, gave 3.7 g. (49%) of yellow crystals, m.p. 149–150°. Mixture with an authentic sample of XII showed no depression of melting point. The infrared spectra were identical.

Anal. Calcd. for C_9OCl_6: C, 32.05; Cl, 63.20. Found: C, 32.07; Cl, 64.00.

Fractions 12 through 65 were combined after evaporation of the solvent to give 3.0 g. (38%) of red needles, m.p. 198.5–199.5°, after recrystallization from hexane. The mixed melting point with an authentic sample of Xa showed no depression. The infrared spectra were identical.

Anal. Calcd. for $C_{11}H_6ONCl_5$: C, 38.26; H, 1.74; Cl, 51.37; N, 4.05. Found: C, 38.18; H, 2.10; Cl, 51.01; N, 4.09.

5,5-Bis-(dimethylamino)-1,2,3,4-tetrachlorocyclopentadiene (VIc).—Dimethylamine hydrochloride (50.4 g., 0.6 mole) and I (27.3 g., 0.1 mole) were mixed in 100 ml. of methanol. After slow addition of potassium hydroxide (33.6 g., 0.6 mole) in 200 ml. of methanol, under cooling in a salt–ice-bath and stirring for 4 days, the potassium chloride was filtered. The methanol was removed and 100 ml. of water and 100 ml. of ether were added to the residue. After shaking, the ether layer was separated, washed with water and dried with Drierite. The ether was removed by evaporation and pentane was added to the residual liquid. Upon cooling, 0.7 g. (2.7%) of colorless crystals of XIII were obtained, m.p. 118–119°, after recrystallization and decolorization with Darco in hexane. The mother liquors were decolorized with Darco at room temperature and the solvent was removed. The light brown liquid was dissolved in pentane and chromatographed on a 20 mm. × 5 cm. column packed with neutral aluminum oxice to give 24.7 g. (85%) of colorless liquid, $n^{20}{}_{\mathrm{D}}$ 1.5400. Cooling in Dry Ice gave colorless prisms of VIc, m.p. 33–34°.

Anal. Calcd. for $C_9H_{12}N_2Cl_4$; C, 37.24; H, 4.14; N, 9.65. Found: C, 37.28: H, 4.26; N, 9.32.

Acid Hydrolysis of VIc.—After slow addition of VIc (2.0 g., 0.007 mole) to 30 ml. of concentrated sulfuric acid at 0°, the mixture was stirred for 0.5 hr., poured onto crushed ice, and extracted with ether. The ether was dried over Drierite and evaporated to give a residue which solidified on addition of hexane. Recrystallization and decolorization in hexane gave 1.2 g. (80%) of VII, m.p. 165°. The mixed melting point with an authentic sample gave no depression.

3-Dimethylamino-2,4,4,5,5-pentachloro-2-cyclopentenone (XIII).—Dimethylamine hydrochloride (2.0 g., 0.025 mole) in 20 ml. of methanol was added to potassium hydroxide (1.4 g., 0.025 mole) in 20 ml. of methanol. The potassium chloride was filtered and the filtrate added to XII (m.p. 28°, 2.5 g., 0.0009 mole), obtained according to Towne and Hill,[12] in 10 ml. of methanol. After standing at 25° for 2 days, the solvent was removed. The residue was treated with 50 ml. of water, extracted with two 25-ml. portions of methylene chloride, and dried over Drierite. The solvent was evaporated and the crystalline residue recrystallized from hexane containing some chloroform to give 2.7 g. (90%) of XIII, m.p. 118–119°.

3-Dimethylamino-2,4,5,6,7-pentachloroindenone (Xa).—Dimethylamine hydrochloride (1.0 g., 0.012 mole) in 20 ml. of methanol and potassium hydroxide (0.5 g., 0.012 mole) in 20 ml. of methanol were mixed and the ensuing potassium chloride was filtered. The filtrate was added slowly to IX (1.0 g., 0.0003 mole), obtained according to Eaton, *et al.*,[10] in 50 ml. of methanol containing 5 ml. of ccetone. The solution immediately became intensely red and after several minutes a red solid started to form. This mixture was stirred for 1 hr. and cooled. Filtration gave 1.0 g. (100%) of red needles of Xa, m.p. 198–199°.

Acid Hydrolysis of Xa.—A mixture of Xa (1.0 g., 0.003 mole) and 25 ml. of concentrated sulfuric acid was heated on a steam-cone for 1 hr. Water was slowly added to the colorless solution, and a yellow solid began to separate. It was filtered through a sintered glass filter, washed free of acid with water, and dried on a clay plate to give 0.9 g. (98%) of 3-hydroxy-2,4,5,6,7-pentachloroindeneone (XI), m.p. 177°; $\lambda_{\max}^{\mathrm{CHCl_3}}$ 2.85(s), 5.85(m), 6.25(s) μ. The mixed melting point with an authentic sample[11] was 177°. The infrared spectrum was identical to that of the authentic sample.

5,7-Methyleneoxy-7-morpholinyl-1,2,3,4-tetrachlorobicyclo[2.2.1]hept-2-ene (XV).—Allyl alcohol (50 ml.) and VIa (10.0 g., 0.027 mole) were mixed and benzene was added until the mixture was homogeneous. After standing for 4 weeks at 25°, the benzene and excess allyl alcohol were removed under reduced pressure to give a red oil. The oil was dissolved in methylene chloride, washed with water several times, dried over Drierite, and the solvent removed. The residue was dissolved in ether, decolorized with Darco and diluted with pentene, but no crystals were obtained on cooling. The solvent was removed to give yellow crystals. Several recrystallizations from methanol gave 4.0 g. (42%) of colorless crystals of XV, m.p. 138°, $\lambda_{\max}^{\mathrm{CHCl_3}}$ 6.24 μ, $\lambda_{\max}^{\mathrm{EtOH}}$ 213 mμ (log ϵ 3.644).

Anal. Calcd. for $C_{12}H_{13}O_2NCl_4$: C, 41.74; H, 3.77; Cl, 41.16; N, 4.08. Found: C, 41.67; H, 4.20; Cl, 40.81; N, 3.81.

***exo*-5-Hydroxymethyl-1,2,3,4-tetrachlorobicyclo[2.2.1]-hept-2-en-7-one(XVI).**—A mixture of XV (1.3 g., 0.033 mole), 50 ml. of concentrated hydrochloric acid and 20 ml. of acetone was heated at reflux for 6 hr. The acetone was evaporated on a steam-cone, the mixture cooled, and extracted with ether. Evaporation of the solvent and recrystallization of the solid residue from hexane–chloroform gave 1.0 g. (96%) of colorless crystals (XVI), m.p. 124.5°; $\lambda_{\max}^{\mathrm{CHCl_3}}$ 2.80(m), 3.00(w) (broad), 3.40(s), 5.45(m), 6.22(s), 6.85(m), 7.25(m) μ; $\lambda_{\max}^{\mathrm{mull}}$ 3.05(s), 6.23(s) μ.

Anal. Calcd. for $C_8H_6O_2Cl_4$: C, 34.78; H, 2.18; Cl, 51.48. Found: C, 34.57; H, 2.44; Cl, 51.22