rapid stream of gaseous hydrogen chloride was passed through the solution for 45 min, the temperature being maintained at or below −20° at all times. After this time a stream of nitrogen was passed through the reaction mixture to flush out the bulk of the hydrogen chloride. The solution was then diluted with 2 l. of chloroform, precooled to −20°, and evaporated at reduced pressure. The residue was taken up in 300 ml of benzene, washed with 250 ml of aqueous 10% sodium carbonate, dried over sodium sulfate, filtered and evaporated. This neutral material was chromatographed on 500 g of Florisil (60/100 mesh). Elution with 1:1 benzene–chloroform gave 9.7 g (52%) of diastereoisomeric product, which crystallized from chloroform–ether as needles, mp 189–190°. While careful chromatography on alumina or silica gel did not separate the isomers, repeated crystallization from chloroform–hexane gave a single racemate: mp 193°; uv max (C_2H_5OH) 268 mμ (ε 4700), 216 (41,700); ir ($CHCl_3$) 2.90 (NH), 5.70 (lactone C=O), 5.85 μ (ester C=O); pmr (pyridine-d_5) τ 1.9–2.6 (m, 4, aromatic), 3.83 (q, 1, J = 6, 10 Hz, CHS), 4.72 (d, 1, J = 10 Hz, CH—CO, 5.0 (m, 1, NH), 5.31 (s, 2, —OCH_2C=), 6.43 [q, 2, J = 18 Hz, SCH_2C(=C)—], 8.60 [s, 9, $OC(CH_3)_3$].

Anal. Calcd for $C_{20}H_{20}N_2O_6S$: C, 57.69; H, 4.80. Found: C, 57.44; H, 5.05.

1,2,5,7-Tetrahydro-α-phthalimido-7-oxo-4H-furo[3,4-*d*][1,3]-thiazine Acetic Acid (XI, R = H).—The crude intermediate, obtained by allowing 1.16 g (4 mmol) of aldehyde [VIII, R = $C(CH_3)_3$] and 1.55 g (4 mmol) of amino lactone I to react in refluxing benzene for 3 hr, was dissolved in 80 ml of nitromethane and cooled to −15°; hydrogen chloride was passed through the solution for 15 min at this temperature; the solution was immediately diluted with 400 ml of ice-cold chloroform and the resulting solution evaporated at reduced pressure below 25°. The residue was taken up in 200 ml of benzene, and extracted with two 60-ml portions of 10% aqueous sodium bicarbonate. The extracts were cooled to 0° and acidified with dilute hydrochloric acid to pH 3 in the presence of 80 ml of chloroform. The aqueous layer was extracted with two additional (80-ml portions of chloroform. The combined chloroform solutions were dried (Na_2SO_4), filtered, and evaporated at reduced pressure below 25°. The resulting crude acid mixture weighed 661 mg (46%) and was immediately dissolved in 10 ml of chloroform and placed in the cold room overnight, producing 239 mg (16.5%) of acid isomer A, mp 162–164° (−CO_2), 248–250° dec. A differential thermal analysis indicated rapid loss of gas (CO_2) with concomitant melting at 167°, resolidification at 175° and finally remelting at 258°, with subsequent decomposition.

Anal. Calcd for $C_{16}H_{12}N_2SO_6$: C, 53.30; H, 3.36; N, 7.78. Found: C, 53.51; H, 3.87; N, 7.66.

The mother liquor on standing deposited 158 mg (11%) of acid isomer B, mp 192–193° (−CO_2) and 245–247° dec. Differential thermal analysis showed major loss of CO_2 and melting at 202° with resolidification at 208° and final melting at 255° with subsequent decomposition. A small depression in the curve at 168° showed the presence of a minor amount of isomer A.

Anal. Calcd for $C_{16}H_{12}N_2SO_6$: C, 53.30; H, 3.36; N, 7.78. Found: C, 53.50; H, 3.32; N, 7.39.

Isomer B was converted in 90% yield by ethereal diazomethane into material of mp 195–212°; recrystallization from acetonitrile gave 70% of pure product, mp 214–218°, identical (mixture melting point, infrared) with the methyl ester previously obtained by direct cyclization.

Registry No.—II, 19289-43-1; IV, 19289-44-2; V, 4019-12-9; IX, R = Me (*trans*), 19289-54-4; IX, R = Me (*cis*), 19289-55-5; XI, R = Me, 19289-46-4; XI, R = *t*-Bu, 17493-47-9; XI, R = H, 17833-99-7; XVII, 19289-57-7.

Polychlorinated Ketones. I. Synthesis and Fragmentation of β,β-Bis(trichloromethyl)-β-propiolactone

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Received August 6, 1968

The uncatalyzed cycloaddition of ketene to hexachloroacetone at 190–200° has given β,β-bis(trichloromethyl)-β-propiolactone (I) in 85% yield. In the presence of catalytic amounts of anhydrous ferric chloride, I underwent facile fragmentation when heated above its melting point to give 1,1,4,4,4-pentachloro-1-buten-3-one (XI), carbon monoxide, and hydrogen chloride. Addition of chlorine to the double bond of XI afforded 1,1,1,3,4,4,4-heptachlorobutan-2-one (XVI) which was readily dehydrochlorinated in the presence of triethylamine to give 1,1,2,4,4,4-hexachloro-1-buten-3-one (XXIV). The structure of lactone I and ketones XI, XVI, and XXIV is supported by physical and chemical investigations.

In connection with our work concerning the polymerization of lactones,[3] we were interested in studying the influence of electronegative groups in the β position of β-lactones on their polymerizability. One of the most widely used methods for the preparation of β-lactones is the reaction of a ketene with a carbonyl compound which requires catalysts in most cases. This reaction and the chemistry of β-lactones have been studied and reviewed in some detail.[4,5] More recently, the cycloaddition of ketene to hexafluoroacetone (ether, −78°, P_2O_5) has been found to give β,β-bis(trifluoromethyl)-β-propiolactone.[6] Similarly, β-trichloromethyl-β-propiolactone (II) was obtained from ketene and chloral at −80° [inert solvents, $BF_3 \cdot O(C_2H_5)_2$].[7] It has also been found that II can be prepared more conveniently from ketene and chloral at room temperature in the absence of solvents and catalysts.[8]

We have now found that when ketene was allowed to react with hexachloroacetone in the absence of catalysts and solvents at 190–200° β,β-bis(trichloromethyl)-β-propiolactone (I) was isolated in 85% yield. Catalysis of the cycloaddition reaction proved unsuccessful. Lewis acids in the presence or absence of a solvent

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[2] Farbenfabriken Bayer, Werk Dormagen, Germany.

[3] H. Ohse and H. Cherdron, *Makromol. Chem.*, **86**, 312 (1965).

[4] H. E. Zaugg, *Org. Reactions*, **8**, 305 (1954).

[5] H. Kröper in Houben-Weyl's "Methoden der organischen Chemie," Vol. 6, Georg Thieme Verlag, Stuttgart, 1963, p 511.

[6] I. L. Knunyants and Yn. A. Cheburkov, *Bull. Acad. Sci., USSR, Div. Chem. Sci.* (Engl. Transl.), 640 (1960).

[7] K. Schimmelschmidt and E. Mundlos, German Patent 1,136,323 (1962); *Chem. Abstr.*, **58**, 3321 (1963).

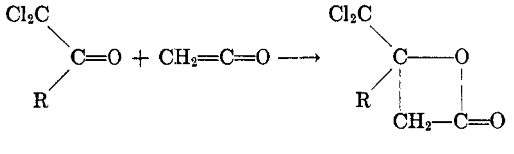
[8] H. Ohse, R. Palm, and H. Cherdron, *Monatsh. Chem.*, **98**, 2138 (1967).

TABLE I

A SUMMARY OF THE EFFECT OF CATALYST AND TEMPERATURE ON THE FORMATION OF β,β-BIS(TRICHLOROMETHYL)-β-PROPIOLACTONE (I)

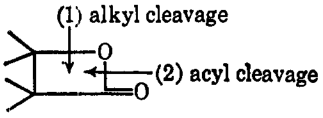
Run	Solvent	Temp, °C	Catalyst	I, % yield
1	CH_2Cl_2	−25	$(CF_3CO_2)_2Zn$	
2	CH_2Cl_2	−25	$BF_3 \cdot O(C_2H_5)_2$	
3		+70	$(CF_3CO_2)_2Zn$	
4		+25		Traces
5		+130		68
6		+150		74
7		+195		85

appear to have no influence on the formation of I at lower temperatures. The products isolated from these runs were hexachloroacetone and diketene. However, the rate of formation of I is largely dependent on the reaction temperature and proceeds with a measurable rate above 100°. As the temperature increases, the yield of I increases, and maximum yields of product are obtained at temperatures between 190 and 200°. The results are listed in Table I.



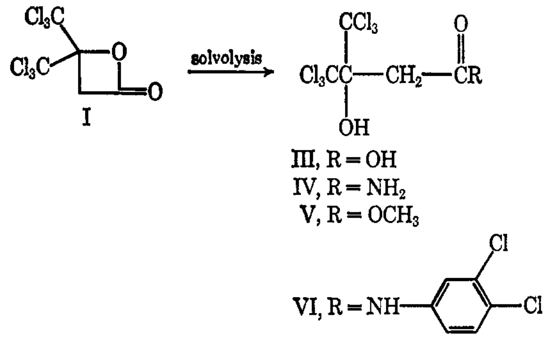
I, R = CCl_3
II, R = H

Compound I is obtained as white crystalline solid with a pleasant odor by distillation under vacuum [bp 103–105° (0.03 mm), mp 52° (from pentane)]. Elemental analysis and spectroscopic data are consistent with the β-lactone structure. Infrared absorption at $\nu_{C=O}$ 1860 and 1895 cm^{-1} confirms the expectation that two electron-withdrawing substituents in the β position in addition to an increased ring strain will result in a further shift toward higher frequencies as compared with γ-lactones.[9a] β-Lactones have properties determined by their ring-opening reactions which may take two different courses: (1) rupture of the bond between oxygen and carbon (alkyl cleavage), and (2) rupture of the bond between oxygen and the carbonyl group (acyl cleavage). Unlike II which reacts with water at 100° to give 4,4,4-trichloro-3-hydroxybutyric acid,[8] I is stable under these conditions.



However, more drastic conditions, *i.e.*, prolonged heating in refluxing 30% sulfuric acid, brings about hydrolysis to 4,4,4-trichloro-3-trichloromethyl-3-hydroxybutyric acid (III). Methanol, ammonia and amines react analogously to give the products of an acyl cleavage of I.

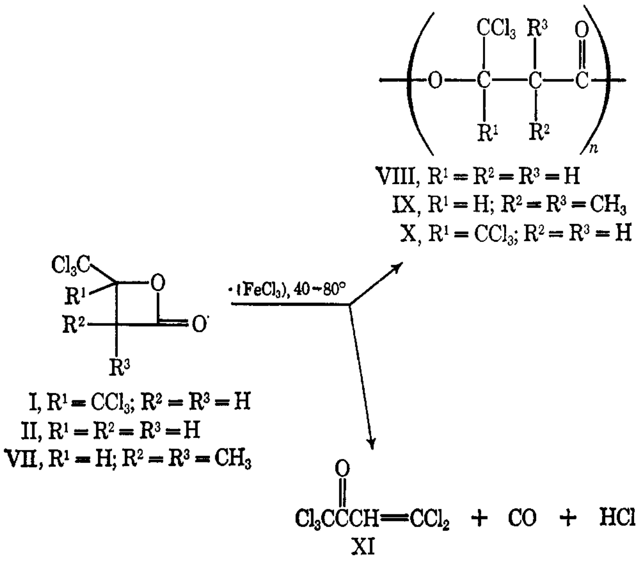
These findings led us to the investigation of a series of catalysts and solvents for the polymerization of I. Initially, the action of anhydrous ferric chloride was studied, since this reagent had successfully effected the polymerization of II and α,α-dimethyl-β-trichloromethyl-β-propiolactone (VII) to give polyesters of general structure VIII and IX, respectively.[10] However, treatment of I with approximately 1 × 10^{-2} mol equiv of anhydrous ferric chloride gave no polyester X. Instead, lactone I decomposed when heated above its melting point to give carbon monoxide and hydrogen chloride (molar ratio 1:1) and 1,1,4,4,4-pentachloro-1-buten-3-one (XI) by a series of logical reactions (see below). After a cursory examination of other possible polymerization initiators,[10] it was found that only anhydrous ferric chloride furnished ketone XI (Scheme I).



I

III, R = OH
IV, R = NH_2
V, R = OCH_3
VI, R = NH—

SCHEME I



VIII, $R^1 = R^2 = R^3 = H$
IX, $R^1 = H$; $R^2 = R^3 = CH_3$
X, $R^1 = CCl_3$; $R^2 = R^3 = H$

I, $R^1 = CCl_3$; $R^2 = R^3 = H$
II, $R^1 = R^2 = R^3 = H$
VII, $R^1 = H$; $R^2 = R^3 = CH_3$

XI

A mechanism that accounts for these observations presumably involves formation of an intermediary complex of I with ferric chloride. In the presumed transition state (XII), it is probable that formation of a relatively stable O–Fe bond is necessary before the electronic shifts involving migration of a trichloromethyl anion from the β-carbon atom into the α position can occur. A logical precursor of XI would be the saturated ketone XIII which easily eliminates hydrogen chloride under the reaction conditions[11] to give XI (Scheme II).

Compound XI is a colorless liquid which has the

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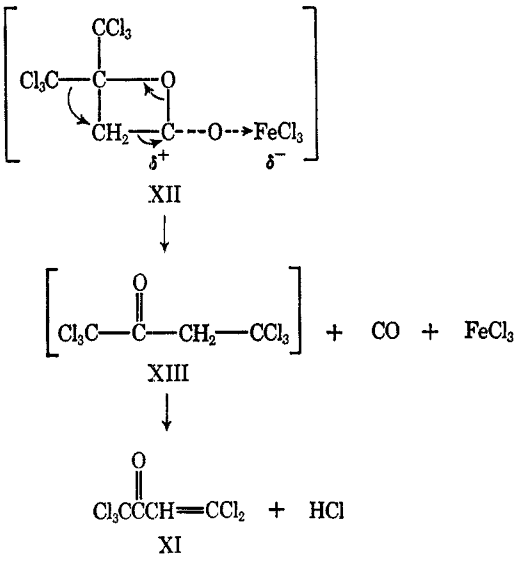
[9] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley & Sons, Inc., New York, N. Y., 1965: (a) p 152; (b) p 115; (c) p 31; (d) p 117.

[10] H. Ohse and H. Cherdron, *Makromol. Chem.*, **108**, 193 (1967).

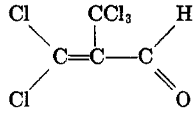
[11] β,β-Dichloroethyl ketones have been isolated and characterized in some cases, but normally they spontaneously eliminate hydrogen chloride on standing: V. Klimko, V. Michalev, and A. Skoldinov, *J. Gen. Chem. USSR*, **27**, 370 (1957); *Chem. Abstr.*, **51**, 15449 (1957).

SCHEME II



empirical formula C_4HCl_5O as calculated from its elemental analysis and its mass spectrum which shows the *m/e* peak at 242 corresponding to the parent peak (M). No evidence for either higher or lower molecular weight impurities was observed in the mass spectrum and by gas chromatographic analyses.

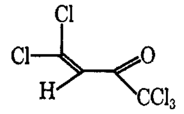
The infrared spectrum of XI shows very clearly the characteristic double-bond absorption at 1562 cm^{-1}, a split carbonyl peak at 1730 and 1705 cm^{-1} and the =CH stretching vibration at 3068 cm^{-1}. It should be noted that similar double-bond absorptions were observed by several authors in infrared spectra of α,β-unsaturated ketones.[12,13] The CH stretching frequency of an aldehyde, *i.e.*, perchloromethacrolein, C_4HCl_5O (XIV), which could also be considered to result from I by



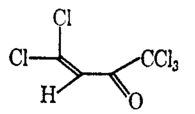
XIV

fragmentation, would be expected near 2900–2700 cm^{-1}.[9b] A splitting of the carbonyl band in the infrared spectra of α,β-unsaturated ketones has been attributed to various factors such as Fermi resonance,[14] rotational isomerism[12b] and to an equilibrium between the *S-cis* and *s-trans* configurations.[15–17] The latter effect does not seem likely for when unstrained coplanar configurations are possible one of these is preferred to the exclusion of the other.[16–18] The minor peak of the split carbonyl band in the infrared spectrum of methyl β,β-dichlorovinyl ketone has been attributed to the first overtone of the very strong C—Cl stretching fundamental.[13]

A Briegleb molecular model of XI shows considerable strain to attainment of coplanarity in the *s-trans* conformation. However, the coplanar *s-cis* structure is achieved without strain. A van der Waals overlap diagram reveals little or no steric hindrance in the *s-cis* configuration, but prohibitive overlap in the *s-trans* conformation.



XI, *s-cis*



s-trans

In the ultraviolet spectrum of XI, maximum absorption is observed at 259 mμ (ϵ 10,492), again indicating a coplanar and highly conjugated system. Methyl vinyl ketone,[18] methyl β-chlorovinyl ketone[18] and methyl β,β-dichlorovinyl ketone[13] absorb at 210 mμ (ϵ 7000), 228 (10,000), and 241 (11,900), respectively. Thus replacement of the methyl group by a trichloromethyl group in methyl β,β-dichlorovinyl ketone had caused a bathochromic shift of 18 mμ.

The nmr spectrum of XI shows one singlet at 7.26 ppm (calcd[19] δ 7.29 ppm); the chemical shift in XIV would be expected to be greater than 9.5 ppm. In summary, we infer from these data that XI exists in the *S-cis* conformation.

Additional evidence for the structure of XI has been obtained by a number of reactions (Scheme III). For example, with phenylhydrazine and XI, pyrazole XV is formed in an exothermic reaction. The initial product, the hydrazone, could not be isolated. Ketone XI does not decolorize bromine in carbon tetrachloride solution, although chlorine is added readily at 0° under irradiation with ultraviolet light to give 1,1,1,3,4,4,4-heptachlorobutan-2-one (XVI). As was to be expected, XI underwent the haloform cleavage fairly easily to give chloroform and β,β-dichloroacrylic acid (XVII). This reaction appears to be the most convenient method of preparation for XVII which is difficult to obtain otherwise.[20] The carbonyl group can be selectively reduced with sodium borohydride forming 1,1,4,4,4-pentachloro-1-buten-3-ol (XVIII). Replacement of the hydroxyl group in XVIII by chlorine with thionyl chloride proceeded smoothly; however, the corresponding chloro compound, XIX, is not obtained. The rearranged material, *trans*-1,1,1,4,4,4-hexachloro-2-butene (XXI), is isolated instead.[21] This reaction presumably involves the cyclic transition state shown in XX. The structure assignment of XXI is based on its infrared spectrum and dipole measurements. For example, the =CH stretching vibration is found at 3085 cm^{-1}; the out-of-plane =CH deformation frequency which is characteristic of a *trans*-olefinic structure[9c] is observed at 945 cm^{-1}. XXI has no dipole moment (measured in benzene) which is consistent with its *trans*-olefinic structure. Chlorination of XXI affords 1,1,1,2,3,4,4,4-octachlorobutane (XXII), whereas treatment with sulfuric acid followed by reaction with ethanol gives diethyl fumarate (XXIII).

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(12) (a) W. R. Benson and A. E. Pohland, *J. Org. Chem.*, **29**, 385 (1964); (b) J. Dabrowski and J. Terpinski, *ibid.*, **31**, 2159 (1966).

(13) S. Searles, Jr., R. A. Sanches, R. L. Sonlen, and D. G. Kundiger, *ibid.*, **32**, 2655 (1967).

(14) K. Noack, *Spectrochim. Acta.*, **18**, 697 (1962).

(15) R. Mecke and K. Noack, *Ber.* **93**, 210 (1960).

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

(17) K. Noack and R. N. Jones, *Can. J. Chem.*, **39**, 2225 (1961).

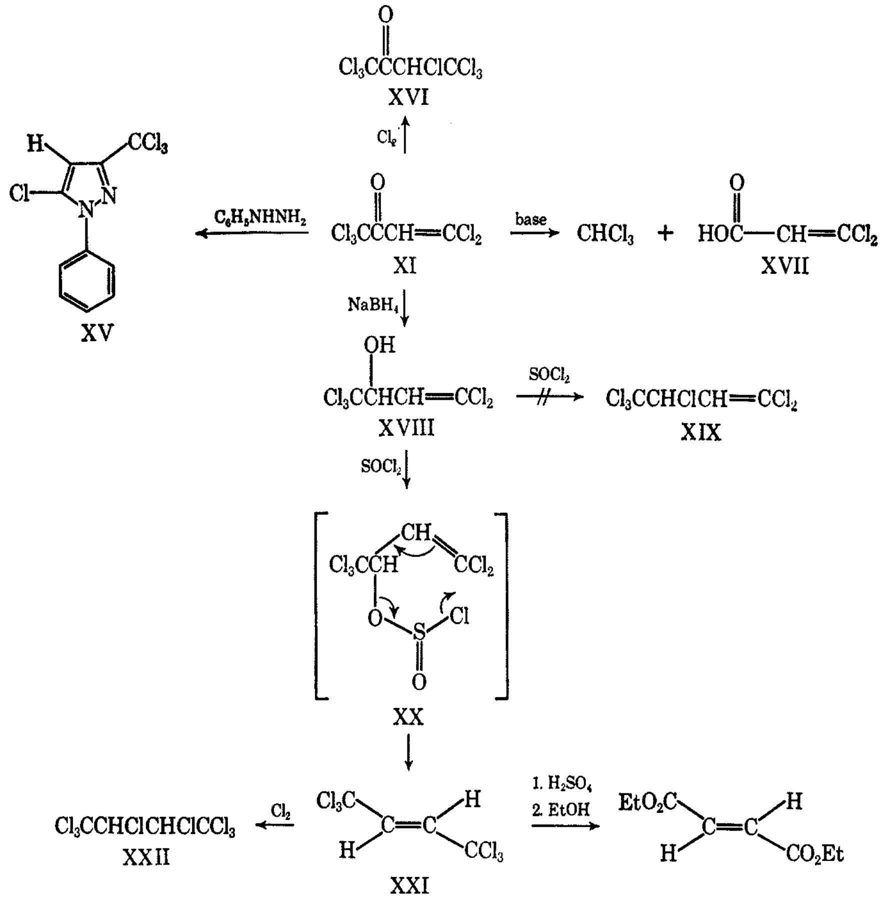
(18) M. Julia, *Ann. Chim.* (Paris), (12) **5**, 595 (1950).

(19) H. Primas, R. Arndt, and R. Ernst, International Meeting of Molecular Spectroscopy, Bologna, 1959.

(20) F. Straus, L. Kollek, and W. Heyn, *Ber.*, **63**, 1877 (1930).

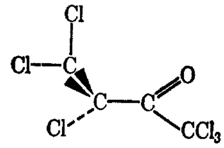
(21) Similar results were obtained by J. Meisenheimer and J. Link, *Ann.*, **479**, 258 (1930), on reaction of thionyl chloride with 1-penten-3-ol and 2-penten-1-ol, respectively.

SCHEME III



Ketone XVI can be readily dehydrochlorinated in the presence of triethylamine at room temperature to give 1,1,2,4,4,4-hexachloro-1-buten-3-one (XXIV) which is identical with the product obtained by dechlorination of octachlorobutanone with triphenylphosphine or a trialkyl phosphite.[22]

The ultraviolet spectrum of ketone XXIV shows maximum absorption at 205 mμ (ε 7139) and 245 (7430). The extinction coefficient is significantly low and presumably due to strain in the coplanar system,[23] or to noncoplanarity. A Briegleb molecular model of XXIV shows considerable steric hindrance to coplanarity in the *s-trans* conformation. A van der Waals overlap diagram shows overlap in both the *S-cis* and *s-trans* conformations. The carbonyl (1745 cm^{-1}) and double-bond (1575 cm^{-1}) absorption bands in the infrared spectrum of XXIV are observed at higher frequencies compared with that of XI indicative of decreased conjugation.[9d] Thus the available evidence indicates a noncoplanar configuration for XXIV induced by the α-chlorine atom.



XXIV

The reactions which were carried out with XXIV are summarized in Scheme IV; the results are similar to those obtained with XI (see Scheme III).

Experimental Section[24]

β,β-Bis(trichloromethyl)-β-propiolactone (I).—In a 1000-ml, four-necked flask fitted with stirrer, thermometer, gas-inlet tube, and reflux condenser protected by a calcium chloride drying tube was placed 503 g (1.9 mol) of hexachloroacetone. The temperature of the condenser was adjusted at −80°, and hexachloroacetone was heated to 190°. Ketene, 84 g (2.0 mol), which was obtained by pyrolysis of diketene, and which had been twice distilled, was introduced through the gas-inlet tube with vigorous stirring. At the beginning, ketene was absorbed rapidly, but later on the consumption of ketene slackened. Stirring was continued for an additional 2 hr at 190° after the addition of ketene was completed. Distillation under vacuum afforded 497 g (85%) of I: bp 103–105° (0.03 mm); mp 52° (from pentane); ir main bands at 1860 and 1895 cm^{-1}.

Anal. Calcd for $C_5H_2Cl_6O_2$: C, 19.6; H, 0.7; Cl, 69.5. Found: C, 19.6; H, 0.8; Cl, 69.9.

4,4,4-Trichloro-3-trichloromethyl-3-hydroxybutyric Acid (III).—A mixture of 50 g (0.163 mol) of I and 1500 ml of 30% sulfuric acid was heated at reflux for 14 hr and cooled. The solid product was suction filtered, washed well with water, dried, and recrys-

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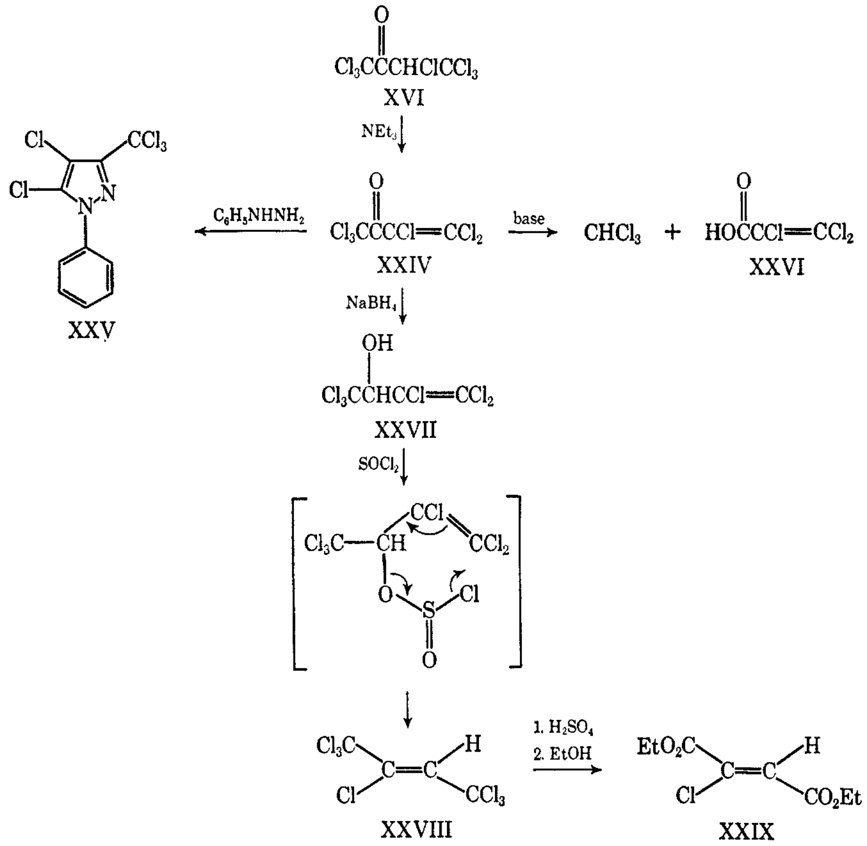
[22] K. Pilgram and H. Ohse, *Angew. Chem. Intern. Ed. Engl.*, **5**, 837 (1966). Attempts by A. Roedig and H. J. Becker [*Ber.*, **89**, 906 (1956)] to prepare XXIV by dechlorination of octachlorobutanone with aluminum filings were unsuccessful.

[23] R. B. Turner and D. M. Voitle, *J. Amer. Chem. Soc.*, **73**, 1403 (1951).

[24] Ultraviolet spectra were recorded with a Cary 14 and Cary 15 recording spectrometers in the region 200–350 and 200–550 mμ, respectively, using methanol as solvent. Infrared spectra were determined on a Perkin-Elmer Model 21 spectrophotometer. Nmr spectra were obtained with a KIS-2 90-Mc spectrometer, using tetramethylsilane as internal standard; chemical shifts (parts per million) are expressed as δ values and coupling constants are given in cycles per second (cps). Melting and boiling points are uncorrected.

SCHEME IV



tallized from hexane to give III: yield 35 g (66.4%); mp 159–160°.

Anal. Calcd for $C_5H_4Cl_6O_3$: C, 18.5; H, 1.2; Cl, 65.6. Found: C, 18.9; H, 1.5; Cl, 65.0.

4,4,4-Trichloro-3-trichloromethyl-3-hydroxybutyramide (IV).—Dry ammonia was bubbled through a solution of I, 3.07 g (0.01 mol), in 50 ml of ether. The mixture was allowed to stand overnight, after which time a white solid had precipitated. Filtration yielded 3.2 g (98.3%) of IV, mp 227–228° (from tetrahydrofuran).

Anal. Calcd for $C_5H_5Cl_6NO_2$: C, 18.6; H, 1.5; Cl, 65.7; N, 4.3. Found: C, 18.8; H, 1.7; Cl, 65.1; N, 4.4.

Methyl 4,4,4-Trichloro-3-trichloromethyl-3-hydroxybutyrate (V).—A solution of 30.7 g (0.1 mol) of I and about 500 mg of *p*-toluenesulfonic acid in 250 ml of methanol was heated to reflux for 6 hr. Most of the excess methanol was removed under vacuum, and the residue was poured into water and extracted several times with ether. The combined ether extractions were dried ($MgSO_4$) and evaporated to dryness. The crystalline residue was recrystallized from petroleum ether to give 25.7 g (76%) of V, mp 55–56°.

Anal. Calcd for $C_6H_6Cl_6O_3$: C, 21.2; H, 1.8; Cl, 62.8. Found: C, 21.2; H, 1.9; Cl, 62.9.

3′,4,4,4,4′-Pentachloro-3-hydroxy-3-(trichloromethyl)butyranilide (VI).—A mixture of 61.4 g (0.2 mol) of I and 32.4 g of 3,4-dichloroaniline (0.2 mol), was heated with stirring at 130–140° over a 1-hr period. Benzene (150 ml) was added. After cooling, 400 ml of pentane was added and white crystalline VI, 42 g (44.8%), mp 212–215°, was collected.

Anal. Calcd for $C_{11}H_7Cl_8NO_2$: Cl, 60.6; N, 3.8. Found: Cl, 60.6; N, 3.2.

1,1,4,4,4-Pentachloro-1-buten-3-one (XI).—In a 500-ml, three-necked flask fitted with stirrer, thermometer, and reflux condenser protected by a calcium chloride drying tube was placed 102.3 g (0.33 mol) of I and 0.5 g of anhydrous ferric chloride. The mixture was heated with stirring in an oil bath at 52–70° until evolution of gas[25] had ceased (*ca.* 7 hr at 70°). The dark reaction mixture was purified by distillation to give 79.2 g (98.3%) of XI: bp 95–96° (13 mm); $n^{20}{}_{D}$ 1.5423; $d^{20}{}_{4}$ 1.6493; colorless liquid; ir (film) (cm^{-1}) main bands at 3068, 1730, 1705, 1562, 1092, 959, 870, 835, 770, 728 cm^{-1}; uv λ_{max} 259 mμ (ε 10,492); nmr (CCl_4) δ 7.26 (s, =CH).

Anal. Calcd for C_4HCl_5O: C, 19.8; H, 0.4; Cl, 73.2. Found: C, 19.7; H, 0.5; Cl, 73.4.

1-Phenyl-5-chloro-3-(trichloromethyl)pyrazole (XV).—To a solution of 24.25 g (0.1 mol) of XI in dry ether, 200 ml, was added dropwise with stirring a solution of 21.6 g (0.2 mol) of phenylhydrazine in 50 ml of dry ether. After the exothermic reaction was completed, 200 ml of water was added to the reaction mixture. The organic layer was washed with water and dried ($CaCl_2$). Ether was removed from the dark red solution to give crude XV which was purified by distillation: bp 112° (0.005 mm); 15.1 g (51%) of XV; $n^{20}{}_{D}$ 1.5995; uv max 400 mμ (ε 91), 311 (132), 239 (11,953); nmr (hexadeuterioacetone) δ 6.66 (pyrazole H) and *ca.* 7.35 (phenyl H).

Anal. Calcd for $C_{10}H_6Cl_4N_2$: C, 40.5; H, 2.0; Cl, 47.9; N, 9.5. Found: C, 40.7; H, 1.8; Cl, 47.9; N, 9.1.

1,1,1,3,4,4,4-Heptachlorobutan-2-one (XVI).—Chlorine, 120 g, was introduced into 400 g (1.65 mol) of XI at 0°. After 3 hr, excess chlorine was removed under vacuum to give 505 g (97.5%) of crude XVI with an estimated purity of 99% (glpc). Distillation under vacuum furnished 485 g (93.7%) of XVI as colorless liquid: bp 110° (9 mm); mp 16°; $n^{20}{}_{D}$ 1.5271; $d^{20}{}_{4}$ 1.7561; nmr (CCl_4) δ 5.31 (s); ir (film) main bands at 2975, 1752, 1300, 1200, 1065, and 770–850 cm^{-1}.

Anal. Calcd for C_4HCl_7O: Cl, 15.3; H, 0.3; Cl, 79.2. Found: C, 15.6; H, 0.4; Cl, 79.1.

β,β-Dichloroacrylic Acid (XVII).—Ketone XI, 2.42 g (0.01 mol), was added dropwise with stirring to 15 ml of 1 *N* sodium hydroxide solution at room temperature. The reaction was exothermic. After 2 hr, chloroform was evaporated and identified by glpc. The aqueous phase was extracted with ether. Acidification of the aqueous solution with concentrated hydrochloric acid gave colorless crystals of crude XVII. Recrystallization from pentane gave 1.03 g (73%) of pure XVII, mp 75–76° (lit.[20] mp 76–77°).

1,1,4,4,4-Pentachloro-1-buten-3-ol (XVIII).—To a solution of 5 g (0.132 mol equiv) of sodium borohydride in 400 ml of water

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(25) The water-soluble fraction of the gas was identified as hydrogen chloride (determined as AgCl). The water-insoluble fraction consisted of carbon monoxide which was identified by mass spectrometry: *m/e* 28 (M).

and 200 ml of ethanol was added dropwise with stirring 121.3 g (0.5 mol) of XI. The temperature was maintained at 10–15° by external cooling with ice water. After the reaction was completed, 400 ml of water was added and the solution was extracted with ether. The combined ether extractions were dried (Na_2SO_4) and evaporated to dryness to give 75 g (61.5%) of crude XVIII as colorless crystallized solid. Recrystallization from pentane afforded 48 g (39.3%) of pure XVIII: mp 80–81°; nmr ($CDCl_3$) δ 3.35 (s, -OH), 4.93 (d, $J = 8.3$, -CH), 6.10 (d, $J = 8.3$, =CH); ir (KBr) main bands at *ca.* 3275, 1625, 1049, 875, 817, and 785 cm^{-1}.

Anal. Calcd for $C_4H_3Cl_5O$: C, 19.6; H, 1.2; Cl, 72.5. Found: C, 19.7; H, 1.4; Cl, 72.7.

trans-**1,1,1,4,4,4-Hexachloro-2-butene (XXI).**—A solution of XVIII, 24.25 g (0.1 mol), in thionyl chloride, 96 g (0.8 mol), was heated to reflux for 5 hr until glpc indicated that the starting material had reacted completely. Excess thionyl chloride was removed under vacuum. The residue was recrystallized from pentane to give 25 g (95%) of XXI as white crystallized solid: mp 81°; nmr (CCl_4) δ 6.57 (s); ir (KBr) main bands at 3085, 1625, 1248, 1090, 1050, 945, 875 and *ca.* 750 cm^{-1}.

Anal. Calcd for $C_4H_2Cl_6$: C, 18.2; H, 0.8; Cl, 81.0. Found: C, 18.4; H, 0.9; Cl, 80.8.

1,1,1,2,3,4,4,4-Octachlorobutane (XXII).—Chlorine was passed into a solution of 3.3 g (12.5 mmol) of XXI in 15 ml of carbon tetrachloride under irradiation with uv light. After 2 hr, carbon tetrachloride was removed and the residue was purified by distillation under vacuum to give 3.85 g (92.1%) of XXII: bp 136° (10 mm); $n^{20}{}_{\rm D}$ 1.5498; $d^{20}{}_4$ 1.8016; colorless viscous oil; ir (film) main bands at 2980, 1275, 1236, 1000, 970, 950 and *ca.* 800 cm^{-1}.

Anal. Calcd for $C_4H_2Cl_8$: C, 14.4; H, 0.6; Cl, 85.0. Found: C, 14.6; H, 0.7; Cl, 85.5.

Diethyl Fumarate (XXIII).—The mixture of 1 g of XXI and 3 ml of concentrated sulfuric acid was heated at 60–80° over a period of 16 hr, when 100 ml of ethanol was added and heating at reflux continued for an additional 24 hr. Ethanol (50 ml) was removed and the resulting reaction mixture was neutralized with aqueous Na_2CO_3. The neutralized solution was extracted several times with ether. The combined ether extractions were dried (Na_2SO_4); the solvent was removed under vacuum and the residue, 0.4 g (61.5%) of crude XXIII, was identified as follows: glpc and ir spectrum of XXIII were identical with those of an authentic sample, nmr (CCl_4) δ 6.79 (lit.[26] δ 6.83).

1,1,2,4,4,4-Hexachloro-1-buten-3-one (XXIV).—A solution of 313.5 g (1 mol) of XVI in 2000 ml of dry ether was prepared. Triethylamine, 101 g (1 mol), dissolved in 100 ml of dry ether was added with stirring at room temperature to the above solution. The reaction mixture was stirred for 15 min and suction filtered. The solid triethylammonium chloride was washed well with dry ether. The combined ether washings and the filtrate were evaporated to give a red liquid which was purified by distillation: bp 34° (0.01 mm); $n^{20}{}_{\rm D}$ 1.5300; $d^{20}{}_4$ 1.6979; yield 267.4 g (96.5%); ir (film) main bands at 1745, 1585, 1488, 1159, 910, 840 and 690 cm^{-1}; uv max 205 mμ (ε 7139) and 245 (7430).

Anal. Calcd for C_4Cl_6O: C, 17.3; H, 0.0; Cl, 76.9. Found: C, 17.7; H, 0.2; Cl, 77.3.

1-Phenyl-4,5-dichloro-3-trichloromethylpyrazole (XXV).—To a solution of XXIV, 27.7 g (0.1 mol), in 200 ml of dry ether was added with stirring dropwise a solution of 21.6 g (0.2 mol) of phenylhydrazine in 50 ml of dry ether. The reaction mixture was stirred for additional 15 min and diluted with 200 ml of water. The organic layer was twice washed with 2 *N* sulfuric acid and dried ($CaCl_2$). Filtration and removal of ether gave a dark red viscous oil which was purified by distillation under vacuum to give 12.5 g (38%) of XXV, a pale yellow liquid: bp 144° (0.02 mm); $n^{20}{}_{\rm D}$ 1.6068; uv max 246 mμ (ε 10,300); nmr δ *ca.* 7.48 (phenyl H).

Anal. Calcd for $C_{10}H_5Cl_5N_2$: C, 36.3; H, 1.5; Cl, 53.7; N, 8.5. Found: C, 36.9; H, 1.7; Cl, 53.5; N, 8.5.

α,β,β-Trichloroacrylic Acid (XXVI).—Ketone XXIV, 2.77 g (0.01 mol), was added dropwise with stirring to 20 ml of 1 *N* sodium hydroxide at room temperature. After 2 hr, the reaction mixture was extracted with ether to remove chloroform. Acidification of the aqueous phase with concentrated hydrochloric acid gave a white crystalline solid which was collected and recrystallized from petroleum ether: yield 1.45 g (82%) of XXIV; mp 74° (lit.[27] mp 74–75°). The ether extract contained chloroform (glpc).

1,1,2,4,4,4-Hexachloro-1-buten-3-ol (XXVII).—To a solution of sodium borohydride, 2 g (52.9 mmol), in 80 ml of ethanol and 160 ml of water was added dropwise with stirring 55.4 g (0.2 mol) of XXIV. The temperature was maintained at 15–20° by external cooling with ice water. The reaction mixture was diluted with 100 ml of water and extracted several times with ether. The combined ether extractions were dried (Na_2SO_4). The solvent was removed under vacuum and the residual liquid was purified by distillation to give 39.8 g (71.6%) of XXVII: colorless liquid; bp 57° (0.01 mm) and 105° (9 mm); $n^{20}{}_{\rm D}$ 1.5486; $d^{20}{}_4$ 1.7326; uv max 211 mμ (ε 9624); nmr (CCl_4) δ 4.14 (-OH), 5.48 (-CH).

Anal. Calcd for $C_4H_2Cl_6O$: C, 17.2; H, 0.7; Cl, 76.3. Found: C, 17.5; H, 1.0; Cl, 76.1.

trans-**1,1,1,2,4,4,4-Heptachloro-2-butene (XXVIII).**—A solution of XXVII, 13.95 g (0.05 mol), in 25 ml of thionyl chloride was heated to reflux for 2 hr. Excess of thionyl chloride was removed under vacuum and the crude reaction product was distilled to give 13.6 g (90.3%) of colorless XXVIII: bp 105° (0.8 mm); $n^{20}{}_{\rm D}$ 1.5568; $d^{20}{}_4$ 1.7812; estimated purity 95.3% (glpc); nmr (CCl_4) δ 6.57 (s).

Anal. Calcd for C_4HCl_7: C, 16.1; H, 0.3; Cl, 83.6. Found: C, 15.8; H, 0.6; Cl, 82.8.

Diethyl Chlorofumarate (XXIX).—A mixture of 8.5 g (28.6 mmol) of XXVIII and 10 ml of concentrated sulfuric acid was heated at 80° for 12 hr. Ethanol, 100 ml, was added and the reaction mixture was heated to reflux for a period of 8 hr. Water, 200 ml, was added to the brown reaction mixture, then the solution was neutralized with aqueous Na_2CO_3 and extracted with ether. The ether extract was dried and evaporated. The residue was distilled to give 2.85 g (48.2%) of XXIX: bp 112° (8 mm); $n^{20}{}_{\rm D}$ 1.4678; estimated purity 95.3% (glpc); nmr (CCl_4) δ 7.10 (s, =CH).

Anal. Calcd for $C_8H_{11}ClO_4$: C, 46.5; H, 5.3; Cl, 17.2. Found: C, 45.8; H, 5.4; Cl, 17.7.

Registry No.—I, 6900-33-0; III, 18767-18-5; IV, 18767-19-6; V, 18767-20-9; VI, 18767-21-0; XI, 15347-86-1; XV, 18767-23-2; XVI, 17334-13-3; XVIII, 18767-25-4; XXI, 18766-87-5; XXII, 18791-19-0; XXIV, 13340-11-9; XXV, 18767-27-6; XXVII, 18767-28-7; XXVIII, 18766-88-6; XXIX, 10302-94-0.

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