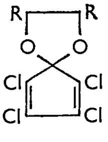
881. *Hexachlorocyclopentadiene. Part IV.*[1,2] *Reaction with 1,2-Diols and a Base at High Temperatures*

By Wen-Hsuan Chang

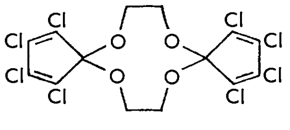
Hexachlorocyclopentadiene reacts with 1,2-diols to give a mixture of at least five compounds, four of which are formed in discrete steps. Structures have been assigned and reaction mechanisms proposed, and some erroneous structures in the literature have been corrected.

HEXACHLOROCYCLOPENTADIENE (I), on treatment with potassium hydroxide and alcohols[3,4] or thiols,[5] yielded 5,5-disubstituted tetrachlorocyclopentadienes. Reaction of (I) with 1,3- and 1,4-diols gave either di(hydroxyalkoxy)tetrachlorocyclopentadienes or polyacetals depending on the amount of glycol used.[2] It reacted with 1,2-glycols under mild conditions to give mainly the simple cyclic acetals (A),[1] which underwent Diels–Alder dimerisation on standing or on warming. With more severe conditions (ethylene glycol, hexachlorocyclopentadiene, and potassium hydroxide at 55° for 2 hr.), it was claimed [4] that the compound (B) was obtained. We repeated the procedure as recommended but isolated some inorganic salt instead of the crystalline C_{14} product, the rest of the product being mainly a mixture of compounds (IVa), (IIIa), and with a compound tentatively assigned either structure (Va) or (Vb). When the reaction was carried out between 80 and 150°, there was obtained additionally a C_{11} compound, tentatively regarded as (VIa).

The above reaction takes place in discrete steps as shown in Chart 1. At room temperature and with the calculated amount of base, the reaction [1] of (I) with ethylene glycol gave (IIIa) and (V) in about 9 : 1 ratio. The reactions [1a] of (I) with propylene glycol or butane-2,3-diol also gave mainly the cyclic acetals (IIIb) and (IIIc). When (IIIa) was again treated with ethylene glycol and potassium hydroxide at 65°, the product was (IVa) in good yield. Reaction of either (I) and (IIIb) with propylene glycol and potassium hydroxide at 55° is comparable, yielding (IVb). Also, (IIIa) was converted at 65° into a similar compound, (VII), when methanol was used in place of the diol.



(A)



(B)

At the still higher temperature of 120°, (IVa) reacts smoothly with ethylene glycol and potassium hydroxide to form (VIa). Treatment of (IVa) with propylene glycol and potassium hydroxide at 120° yielded the homologue (VIb). When (IVb) was treated with

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[1] (*a*) Part III, W.-H. Chang, *J.*, 1965, 2305; (*b*) W.-H. Chang, *Chem. and Ind.*, 1964, 709, is considered Part I.

[2] Part II, W.-H. Chang, *Chem. and Ind.*, 1964, 1491.

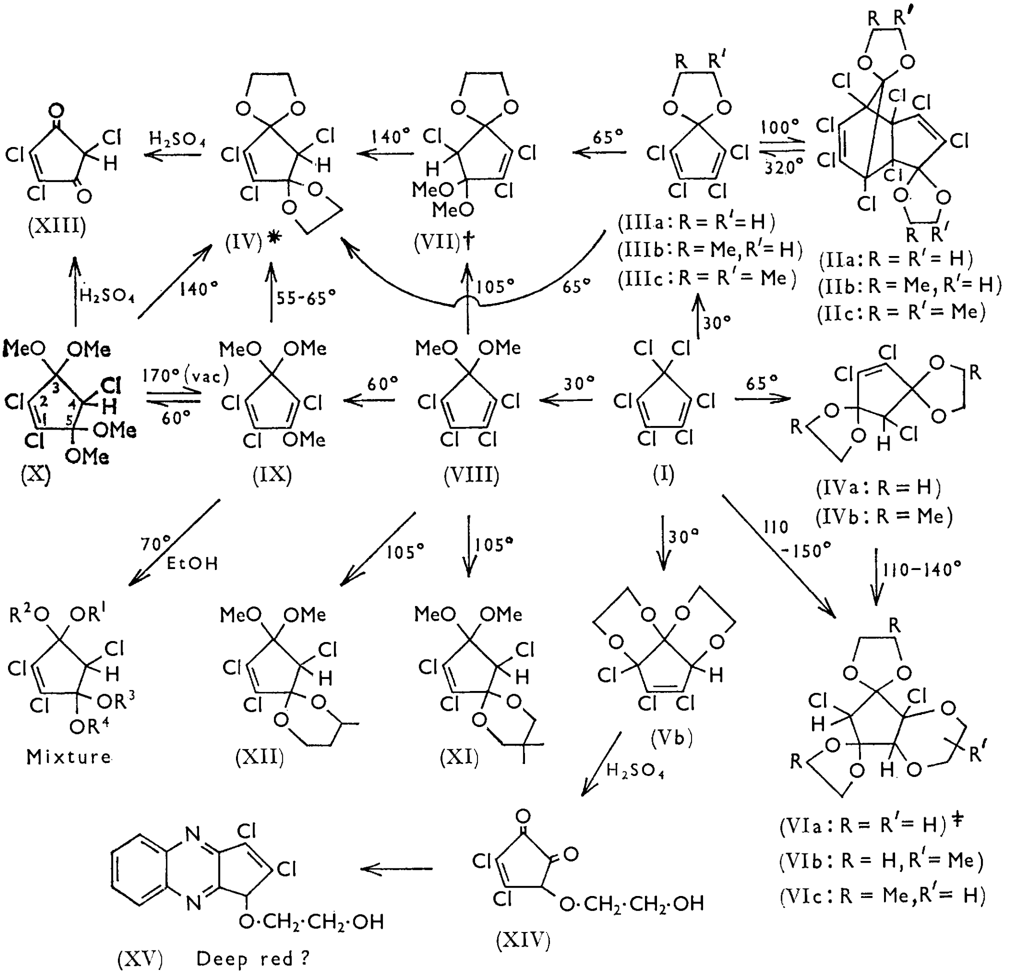
[3] J. A. Krynitsky and R. W. Bost, *J. Amer. Chem. Soc.*, 1947, **69**, 1918.

[4] J. S. Newcomer and E. T. McBee, *J. Amer. Chem. Soc.*, 1949, **71**, 946.

[5] E. P. Ordas, U.S.P. 2,697,103 (1954).

ethylene glycol and potassium hydroxide, the reaction gave rise to (VIc). Some unused (IVb) usually contaminated the (VIc), but it was separable by high temperature gas-liquid chromatography (g.l.c.). Thus, a sample of b. p. 120—126°/0·1 mm. was shown by g.l.c. to consist of (VIc) and (IVb) in a 3 : 2 ratio.

Chart I



(IV) * 36% from (IX), 60% from (IIIa) 95% from (X), 95% from (VIIb).
(VII) † 63% from (IIIa), 91% from (VIII).
(VIa) ‡ 75% from (IVa).

The reaction of methanolic potassium hydroxide with 1,2,3,4-tetrachloro-5,5-dimethoxycyclopentadiene (VIII) yielded mainly 1,2,4-trichloro-3,5,5-trimethoxycyclopentadiene (IX),* which was changed quantitatively into 1,2,4-trichloro-3,3,5,5-tetramethoxycyclopentene (X)† when refluxed simply with an excess of methanol. [This differs from ref. 6 where it is stated that no reaction occurred on refluxing with (IX) methanol in the absence of bases.] Compound (VIII) was more stable toward bases than (IIIa); it gave

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* After this phase of the work was completed, the preparation of this compound was published,[6] but the structure of (IX) and (X) were incorrectly assigned (*vide infra*).

† Compound (X) gave two different infrared spectra in Nujol mulls, but the same spectrum in chloroform, indicating two crystalline forms.

[6] E. T. McBee, D. L. Crain, D. R. Crain, L. R. Belohlav, and H. P. Braendlin, *J. Amer. Chem. Soc.*, 1962, **84**, 3557.

no reaction with ethylene glycol and potassium hydroxide at 70°, but did react at 105° to generate (VII) in 91% yield. It was helpful in the assignment of structures to discover that the addition of alcohols to (IX) was reversible, as shown by the following examples. 1. When (IX) was heated with ethylene glycol alone at 55—65° for 16·5 hr. it gave a 36% yield of (IVa). 2. Pyrolysis of (X) at 167° for 48 hr. *in vacuo* yielded (IX) in 17% yield; the rest of (X) was recovered. 3. On heating (IV) with ethanol there resulted a mixture of many products (g.l.c.), which were probably formed by reversible alcohol addition and elimination; this interpretation is supported by the infrared spectrum and by the following findings. 4. When (VII) was heated with ethylene glycol at 140° for 30 min., the methanol was displaced and removed, and (IVa) was obtained in good yield. 5. The same result was obtained when (X) was heated with ethylene glycol.

Since the addition of alcohols to (IX) had been shown to be reversible, it was expected that (VIII) would react with potassium hydroxide and other glycols to give only low yields of pure products. Actually (VIII) reacted with 2,2-dimethylpropane-1,3-diol and potassium hydroxide to give only a 38% yield of compound (XI). Compound (VIII) reacted similarly with butane-1,3-diol to yield compound (XI), and similarly with butane-1,3-diol to yield (XII).

Discussion.—The structures of (IIa—c) and (IIIa—c) have been proved previously.[1] Proof of structure of (IVa) is as follows. Elemental analysis and molecular weight determination indicated the empirical formula, $C_9H_9Cl_3O_4$. The infrared spectrum (Table 1) indicated the presence of an αβ-dichloro-substituted double bond[6] and the absence of hydroxyl and carbonyl groups; this also suggests that the four oxygen atoms must be present in acetal linkages. The ultraviolet spectrum (Table 1) shows the characteristic absorption[6,7] of a cyclopentene and demonstrates the absence of conjugated double bonds; this is supported by the fact that it was impossible to obtain a Diels–Alder adduct when (IVa) was heated with maleic anhydride, and that it was not possible to add bromine (in carbon tetrachloride) at 35°. Compound (IVa) was hydrolysed by concentrated sulphuric acid to the known compound * (XIII), indicating that the two ethylenedioxy-groups of (IVa) are bonded to 1,3-carbon atoms to form either 5- or 7-membered oxygen-containing rings. Since the structure of (IIIa) is unambiguously proved,[1a] the synthesis of (IVa) from (IIIa) suggests that (IVa) contains at least one *gem*-ethylenedioxy-group. From the above evidence, the only reasonable structure for (IVa) is that given in Chart 1. The structure is further confirmed by the n.m.r. spectrum which shows three peaks (the

TABLE 1

			Found (%)			Required (%)					
	M. p.	B. p./mm.	C	H	Cl	C	H	Cl	λ (mμ)	ε	$\lambda_{max.}$ (μ)
(IVa)	107—108°	120—130°/ 0·04	37·95	3·45	37·5	37·6	3·15	37·0	215sh	4850	6·10
(IVb)	Oil	102/0·038 ($n_D^{24·5}$ 1·5098)	41·85	4·15	33·7	41·85	4·15	33·7	298sh 215sh	298 6110	6·11
(VII)	67·5—68·5	88—90/ 0·03—0·05	37·75	3·85	36·9	37·35	3·85	36·75	250 (max.) 237 (min.) 215sh	377 358 6050	6·11
(X)	57	88—92/0·15	Previously reported[6]						250 (max.) 237 (min.) 215sh	450 349 6750	6·14
(XI)	86—88 (clear at 90)	130—140/ 0·1	43·5	5·15	30·7	43·45	5·15	32·1	251 (max.) 233 (min.) 215sh	862 572 6900	6·12
(XII)	115—116	124—126/ 0·05—0·15	41·7	4·9	33·3	41·75	4·9	33·3	215sh	8090	6·19

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* The structure of (XIII) was incorrectly assigned by Prins[8] and it was shown to be 2,4,5-trichlorocyclopent-4-ene-1,3-dione.[9]

[7] E. T. McBee, J. O. Stoffer, and H. P. Braendlin, *J. Amer. Chem. Soc.*, 1962, **84**, 4540.

H. J. Prins, *Rec. Trav. chim.*, 1946, **65**, 455.

[9] A. Roedig and G. Markl, *Annalen*, 1960, **636**, 1.

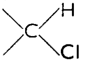
TABLE 2

	M. p.	B. p./mm.	Yield (%)	Found (%) C	Found (%) H	Found (%) Cl	Required (%) C	Required (%) H	Required (%) Cl
(VIa)	142—143°	150°/0·018	75	41·9	4·3	22·2	42·2	4·5	22·65
(VIb)	113—115	146/0·07	34·8	44·25	4·95	21·7	44·2	4·6	21·9
(VIc) †	—	120—126/0·10	60 †	44·35	4·95	25·4	44·3	4·7	26·0

† A mixture of (VIc) (60%) and starting material (IVb).

TABLE 3

Nuclear magnetic resonance spectra (τ values)

		Grouping			
	Solvent		1,3-Dioxolan	*gem*-Dimethoxy	1,4-Dioxan
(IIIa) ‡	?	—	5·73	—	—
(IVa)	$CDCl_3$	5·61	5·80, 5·81	—	—
(VII)	$CDCl_3$	5·65	5·79, 5·82	6·39, 6·63	—
(X)	$CDCl_3$	5·68	—	6·39, 6·63	—
(V)	$CDCl_3$	5·08	—	—	6·39 to 5·72 >30 peaks
(VIa)	CCl_4	5·75	5·95, 5·98, 6·03, 6·07	—	6·25—5·75 multiplet

‡ Reported by D. M. Lemal, E. P. Gosselink, and A. Ault, *Tetrahedron Letters*, 1964, 579.

last two only partially resolved) (Table 3). The intensity ratio of the first peak to the last two peaks was 1 : 8, and the peaks are assigned to the protons as shown in Table 3 by comparison with data in the literature.* This rules out [11] the possibility of dioxan rings or seven-membered ring structures.

The structure of (X) was erroneously formulated [6] as that of 1,2,3-trichloro-4,4,5,5-tetramethoxycyclopentene, based on the erroneous structure of (XIII) assigned by Prins.[8] It was shown to be 1,2,4-trichloro-3,3,5,5-tetramethoxycyclopentene from its correlation with (IVa) [interconversion of (XIII) into (IVa) in 95% yield] and by the n.m.r. spectrum (Table 3). The methoxyl hydrogen resonances of 1,2,3-trichloro-4,4,5,5-tetramethoxycyclopentene would be expected to give a set of quadruple bands. Actually, the n.m.r. spectrum of (X) gives only three peaks, while the methoxyl hydrogen resonances contribute only two identical peaks at 6·39 and 6·63τ, indicating the presence of only two kinds of methoxyl group.

The structure of (IX) was also erroneously assigned.[6] Based on the reversibility of the transformation of (X) and (IX), compound (IX) must be 1,2,4-trichloro-3,5,5-trimethoxycyclopenta-1,3-diene.

The structure of (VII) is assigned by comparison of its physical properties with those of (IVa) and (X), and also by the methods for its synthesis (Chart 1). The isolation of only one product from the reactions of (IIIa) and (VIII) further supports the assigned structure. Structures (IVb), (XI), and (XII) were assigned by analogy with the above compounds.

From the n.m.r. spectrum of (VII), one can conclude that the three hydrogen atoms in each methyl group are equivalent, and thus their resonances are shown by the two identical peaks at 6·39 and 6·63τ. This further suggests that each of the two absorption peaks in (X) must be caused by resonance of the six hydrogen atoms of the two methoxyl groups bonded to the different carbon atoms. Since a chlorine atom has a higher shielding constant than a hydrogen atom [12] the peak (at 5·39τ) with higher chemical shift is probably

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* The chemical shift [10] for cyclopentyl chloride is reported to be 4·31 p.p.m.

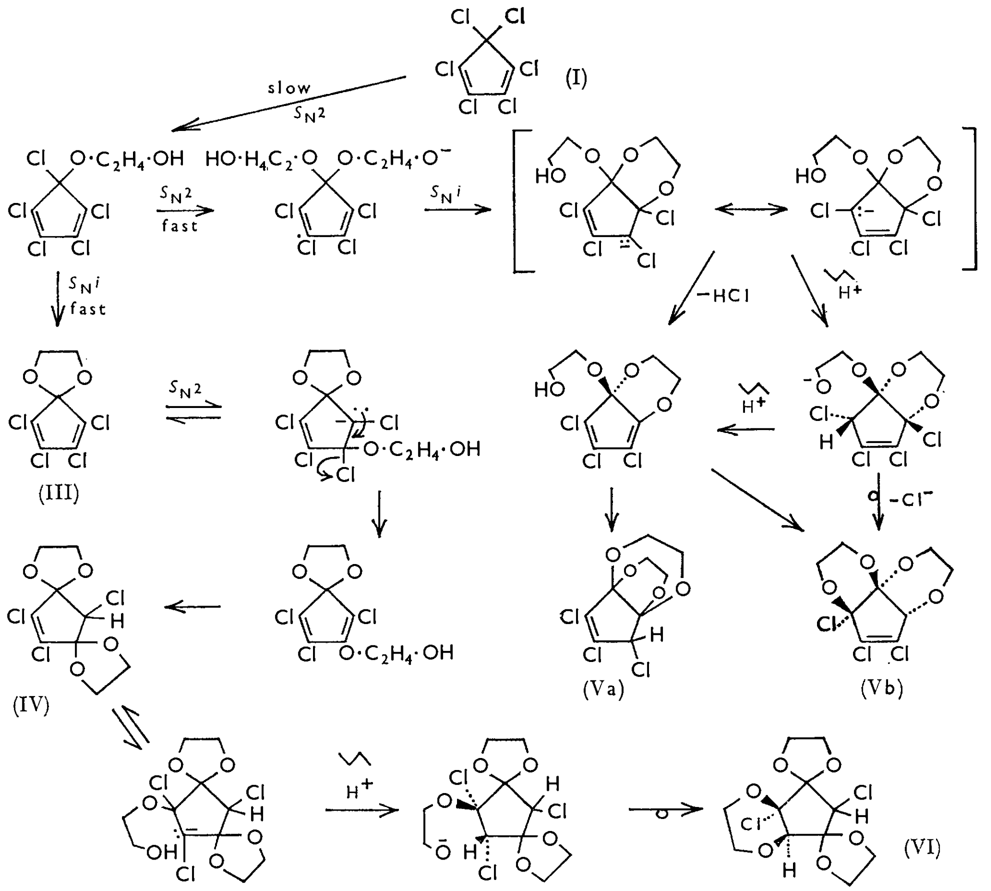
[10] A. A. Bothner-By and A. Naar-Colin, *J. Amer. Chem. Soc.*, 1958, **80**, 1728.

[11] A. E. Caspi, Th. A. Wittstruck, and D. M. Piatak, *J. Org. Chem.*, 1962, **27**, 3183; E. Caspi, Th. A. Wittstruck, and N. Grover, *ibid.*, 1962, **28**, 763; E. Caspi, H. Zajac, and Th. A. Wittstruck, *ibid.*, 1964, **29**, 640.

[12] J. N. Shoolery, Technical Information Bulletin, Varian Associates, Palo Alto, California, 1959, **2**, No. 3, as quoted by L. M. Jackman in " Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon, New York, 1959.

due to the resonance absorption of the hydrogen atoms *cis* to the chlorine atom at C-4. The peak at 6·63τ is probably caused by the absorption of the methoxyl hydrogens *cis* to the hydrogen atom at C-4. The resonance ABCD spectrum due to the hydrogen atoms on the ethylenedioxy-groups must be an incompletely resolved multiplet.

Chart 2



Structure (V) is suggested tentatively, based on the elemental analysis, and infrared and ultraviolet spectra. The more than thirty peaks from 6·39 to 5·72τ in its n.m.r. spectrum indicated the absence[11] of a *gem*-ethylenedioxy-group, but the presence of either rigid dioxan or seven-membered oxygen-containing rings;[11] of these two, only the dioxan rings seemed likely [(Va) and (Vb) in Chart 2].

The tentative assignment of structures (VIa) and (VIb) is based principally on the method of preparation, molecular weight, infrared spectrum (no absorption at 6·0—6·3μ), and ultraviolet spectrum (no absorption). The n.m.r. spectrum of (VIa) showed a major singlet at 5·75τ for the resonance of the two methine hydrogen atoms (overlapping is probably accidental). The four major peaks (symmetrical A_2B_2 pattern) within the more than eleven peaks at 5·95, 5·98, 6·03, 6·07τ may be assigned to the hydrogens of the two *gem*-ethylenedioxy-groups.[11] Because the molecule is highly unsymmetrical, the above splitting is expected.

The mechanism of the reaction is represented in simplified form in Chart 2.

EXPERIMENTAL

Columns (2 ft. × ¼ in.) for gas chromatography were packed with Apeizon L on Chromosorb W unless it is stated otherwise.

Reaction of Ethylene Glycol, Potassium Hydroxide, and Hexachlorocyclopentadiene.—Newcomer and McBee's procedure [4] was followed, but with different findings. Ethylene glycol (750 g., 12·1 moles) containing potassium hydroxide (85%; 600 g., 10·7 moles) was added dropwise at 55° to hexachlorocyclopentadiene (2 moles) during 2 hr. The organic layer which separated was dissolved in hexane. Upon cooling to −78°, crystalline inorganic salt separated. After 4 days at −10°, solid (40·0 g.) separated from the filtrate. This was repeatedly recrystallised from benzene and ligroin (b. p. 86—100°), to give (IVa) (Table 1) [*M*(cryoscopy in glacial acetic acid), 322, 320, 317; (osmometry), 306. Calc., 287·5]. Bromine and iodine unsaturation tests were negative. It was distilled [most of (IIIa) dimerised, as shown by the infrared spectrum], to give fractions: 1, b. p. 25—78°/0·50—0·16 mm.; 2, b. p. 78—80°/0·13 mm., solidified on standing; 3, b. p. 90—130°/0·01 mm., semi-solid; 4, residue. Fraction 1 was redistilled, and (I) (134 g.) was recovered. Fraction 2 was mixed with hexane and cooled at −10°, to give a solid (35 g.), m. p. 45—62°. Repeated recrystallisation from ether–hexane without heating gave (IIIa) in low yield. Fractions 3 and 4 and all the filtration residues were mixed and extracted with acetone. There was 90 g. of insoluble solid, m. p. 262—272°. Part of it was recrystallised from chloroform to give (IIa). After removal of acetone, the above filtrate was again distilled, b. p. 120—132°/0·01 mm. This gave (IVa) (88·5 g.) after repeated recrystallisation from ether–hexane. The mother-liquor was then chromatographed on wet-packed alumina (30 × 2·54 cm.). Elution was with hexane–carbon tetrachloride (4 : 1 v/v) (500 ml.), then with 3 : 2 v/v (500 ml.), to give mainly (IVa) as shown by g.l.c. Elution was next with carbon tetrachloride–ether–hexane (1 : 3 : 7) (500 ml.), and the residue from this was distilled, b. p. 140°/0·10 mm. It gave, after eight recrystallisations from ether–hexane, (V), m. p. 79·5—80° [Found: C, 37·85; H, 3·2; Cl, 36·65%; *M* (osmometry), 298. Calc. for $C_9H_9Cl_3O_4$: C, 37·6; H, 3·15; Cl, 37·0%; *M*, 288].

6,12,13-*Trichloro*-1,4,8,11-*tetraoxadispiro*[4,1,4,2]*tridec*-12-*ene* (IVa).—(*a*) Compound (IX) (26·0 g., 0·10 mole) and ethylene glycol (25·0 g., 0·40 mole) were heated at 55—65° for 16½ hr. The oil, precipitated by water, was dissolved in ether, washed three times with water, dried, and distilled, b. p. 89—114°/0·04 mm. (13·2 g.), to yield (IVa) (11·6 g., 36%).

(*b*) To a mixture of ethylene glycol (74·4 g., 1·20 moles) and potassium hydroxide (85%; 31·2 g., 0·60 mole) was slowly added on ether solution of (IIIa) (52·4 g., 0·20 mole) while the ether was removed continuously at 65°/20 mm. The mixture was stirred at 65—70° for 22½ hr.; the crude product was precipitated by water and filtered off. The solid was distilled to give (IIIa) (34·4 g., 60%), b. p. 120—130°/0·04 mm., and (VIa) (3·0 g.).

(*c*) A mixture of 2·0 g. of either (VII) or (X) and 2·0 ml. of ethylene glycol, heated in an oil-bath at 140° for ½ hr., gave (IVa) (1·9 g.).

6,12,13-*Trichloro*-2,9-*dimethyl*-1,4,8,11-*tetraoxadispiro*[4,1,4,2]*tridec*-12-*ene* (IVb).—(*a*) To a refluxing (62°) mixture of propylene glycol (920·8 g., 12·1 moles), potassium hydroxide (85%; 600 g., 10·7 moles), dimethoxyethane (575 ml.), and pentane (250 ml.), (I) (54·6 g., 2·0 moles) was added dropwise. The mixture was stirred and refluxed overnight (water removed in Dean–Stark apparatus). The product was neutralised with dilute hydrochloric acid, washed with water, dried, and distilled twice (Table 1).

(*b*) Potassium hydroxide (4 g.) was dissolved in propylene glycol (100 ml.) at 80°. To this was added a solution of (IIIb) (4·95 g.) in 1,2-dimethoxyethane (5·0 ml.), and the mixture was stirred at 60° for 20 hr., to yield (IVb) (4·0 g., 72·5%).

6,7,9-*Trichloro*-8,8-*dimethoxy*-1,4-*dioxaspiro*[4,4]*non*-6-*ene* (VII).—(*a*) To a mixture of methanol (54·4 g., 1·70 moles) and potassium hydroxide (85%; 31·2 g., 0·60 mole) at 65—70° was added dropwise (IIa) (52·4 g., 0·20 mole) in dimethoxyethane (60 ml.), and the mixture stirred for 2 hr. The product was washed with water, dried, distilled, and recrystallised three times from ligroin, to give (VII) (29·5 g.) (Table 1). The filtrate was shown by g.l.c. to contain (VII) (7·96 g.) (total yield, 37·46 g., 63%), unchanged (IIa) (6·15 g.), and two other by-products (1·35 and 1·60 g.).

(*b*) Compound (VIII) (52·8 g., 0·2 mole) was added dropwise to ethylene glycol (74·4 g., 1·20 moles) and potassium hydroxide (85%; 31·2 g., 0·60 mole) at 105° during 2 hr. Working-up gave crystalline (VII) (48·5 g.), and a further 4·95 g. in the filtrate (shown by g.l.c.) (total yield 91%).

1,2,4-*Trichloro*-3,3-*dimethoxy*-8,8-*dimethyl*-6,10-*dioxaspiro*[4,5]*dec*-1-*ene* (XI).—Compound (VIII) (53 g., 0·20 mole) was added dropwise during 20 min. to a mixture (85°) of 2,2-dimethoxypropane-1,3-diol (125 g., 1·20 moles), potassium hydroxide (85%; 40 g., 0·60 mole), and 1,2-dimethoxyethane (200 ml.). The mixture was stirred for 12 hr., water added, the product dissolved in ether, washed with sodium chloride solution until neutral, dried, and distilled, to give two fractions, b. p. 86—180°/0·05 mm. (45 g.), and b. p. 180—220° (12·2 g.). The latter gave (XI) (16·0 g.) (from pentane), and the filtrate was redistilled to give a further 11 g., b. p. 130—140°/0·1 mm. They were mixed and recrystallised several times from hexane, to give (XI) (19 g., 28·7%) and a semi-solid (8·2 g.) which was not further purified.

1,2,4-*Trichloro*-3,3-*dimethoxy*-7-*methyl*-6,10-*dioxaspiro*[4,5]*dec*-1-*ene* (XII).—The procedure was the same as for compound (XI), but with butane-1,3-diol. The redistilled fraction (31·6 g.), b. p. 126—146°, showed hydroxyl absorption in the infrared (2·90 μ), and that for substituted conjugated double bonds (6·10s, sharp; 6·22w, sharp). Redistillation gave 20·0 g., b. p. 80—150°/0·10 mm., which after several recrystallisations from ether–ligroin (b. p. 86—100°) gave (XII) (6·5 g.) (no OH absorption, but one peak at 6·12 μ indicating C=C); it was not certain whether the hydroxy-compound had been removed or cyclised in the purification.

1,8-*Dichloro*-7,7 : 9,9-*bisethylenedioxy*-2,5-*dioxabicyclo*[4,3,0]*nonane* (VIa).—To a solution of ethylene glycol (74·4 g., 1·2 moles) and potassium hydroxide (85%; 31·2 g., 0·6 mole), at 117—120°, (IVa) (57·2 g., 0·20 mole) dissolved in 1,2-dimethoxyethane (100 ml.) was added dropwise while the low-boiling solvent was continuously distilled off. The solution was refluxed at 120° for 8 hr., water was added, and filtration yielded (VIa) (36 g.), m. p. 114—130°, which was distilled and recrystallised from acetone–methanol and acetone–ligroin (Table 2) [Found: *M*(osmometry), 329. Calc., 313]. When the reaction was carried out at 143° for 3 hr., the yield of (VIa) was 4·5 g.

Compound (VIb).—The method was as for (VIa), with (IIIa) (0·10 mole), propylene glycol (0·60 mole), potassium hydroxide (0·30 mole), and 1,2-dimethoxyethane (50 ml.). The crude distilled product (11·4 g.) was redistilled, b. p. 146°/0·07 mm. (10·3 g., 34·8%). It was shown to be pure (g.l.c.), and was recrystallised from ether–methanol to give (VIb) (Table 2).

Compound (VIc).—Compound (IVb) (0·10 mole) was added to ethylene glycol (0·60 mole) and potassium hydroxide (0·30 mole) at 135°. The mixture was stirred at 135—140° for 9 hr., and the oily product was worked up (as above) to give crude (VIc), b. p. 120—126°/0·10 mm., $n_D^{24\cdot5}$ 1·4985, shown by g.l.c. to be mainly a mixture of starting material (40%) and (VIc) (60%) (Found: C, 44·35; H, 4·95; Cl, 25·4. Calc. for starting material, $C_{11}H_{13}Cl_3O_4$: C, 41·85; H, 4·15; Cl, 33·7. Calc. for (VIc), $C_{13}H_{17}Cl_2O_6$: C, 45·9; H, 5·05; Cl, 20·85. Calc. for a 40 : 60 mixture of the two: C, 44·3; H, 4·7; Cl, 26·0%).

1,2,4-*Trichloro*-3,5,5-*trimethoxycyclopentadiene* (IX).—Compound (VIII) (120 g., 0·455 mole) was added dropwise to a refluxing mixture of methanol (200 ml.) and potassium hydroxide (85%; 61·0 g., 0·91 mole), and the mixture was refluxed for 20 hr. at 74°, washed, and distilled. It was fractionated carefully at 0·15 mm. through a 30-cm. column to give many fractions. One fraction, b. p. 74° (9·0 g.), n_D^{26} 1·5132 was shown by g.l.c. to be pure (IX), $\lambda_{\text{max.}}$ ($\mathrm{Pr^iOH}$) 307 mμ (log ε 3·336), $\lambda_{\text{min.}}$ 262 mμ (log ε 2·713) (lit.,[6] $\lambda_{\text{max.}}$ 310 mμ, log ε 3·282, n_D^{20} 1·5170).

1,2,4-*Trichloro*-3,3,5,5-*tetramethoxycyclopentene* (X).—A mixture of (IX) (20 g., 0·074 mole) and methanol (24 g., 0·75 mole) was refluxed for 24 hr., to yield (X) (21·2 g.).

Pyrolysis of Compound (X).—Compound (X) (5·8 g.) was refluxed at 126—129°/1·5 mm. for 42 hr. The product contained starting material (98%) and (IX) (2%), as shown by g.l.c. It was again refluxed at 167°/20 mm. for 48 hr., to give (IX) (16·7%) and (X) (83 %).

Acid Hydrolysis of Compound (IVa).—Cold conc. sulphuric acid (50 ml.) was added to molten (IVa) (8·0 g., 0·0278 mole); the temperature rose to 50°. The mixture was stirred at 50° for 15 min., poured on ice, and extracted with ether, and the extract was washed with water and dried, to yield a dark oily residue containing the crude compound (XIII). This was dissolved in conc. hydrochloric acid (50 ml.) while sodium chlorate (2·0 g.) was added in portions at 40°, and stirring was continued at 40° for ½ hr. The product was steam-distilled, and extraction with chloroform gave compound (XIV) (1·42 g.).

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