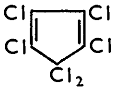
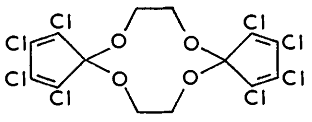
424. *Reactions of Hexachlorocyclopentadiene. Part III.*[1,2] *2′,3′,4′,5′-Tetrachloro-1,3-dioxolan-2-spirocyclopenta-2′,4′-dienes and their Adducts*

By WEN-HSUAN CHANG

Some 2′,3′,4′,5′-tetrachloro-1,3-dioxolan-2-spirocyclopenta-2′,4′-dienes have been prepared. The dimers and adducts are also described. The ease with which 1,2,3,4-tetrachlorocyclopentadienes undergo the Diels–Alder reaction is rationalised in terms of steric and " inverse " electronic effects.

REACTION of hexachlorocyclopentadiene (I) with alcohols and thiols in the presence of a base is known to give ketals[3,4] and thioketals,[5] whilst reaction with 1,3- and 1,4-diols gives mainly bishydroxyalkoxycyclopentadienes and polyketals.[2] In contrast, the reaction of ethylene glycol, potassium hydroxide, and compound (I) was claimed[4] to give compound (A), 2,2″,3,3″,4,4″,5,5″-octachlorocyclopentene-1-spiro-1′-2′,5′,7′,10′-tetraoxecan-6′-spiro-1″-cyclopenta-2,2″,4,4″-tetraene. In our hands[1] this result could not be repeated but, under different conditions, the reaction gave 2′,3′,4′,5′-tetrachloro-1,3-dioxolan-2-spirocyclopenta-2′,4′-diene (IIa) in 90% yield. A by-product melting at 79·5—80° was obtained in <10% yield (calculated for $C_9H_9Cl_3O_4$) (its structure will be discussed in a forthcoming publication). Compound (I) also reacted with propane-1,2-diol to give 2′,3′,4′,5′-tetrachloro-4-methyl-1,3-dioxolan-2-spirocyclopenta-2′,4′-diene (IIb) in lower yield, and with butane-2,3-diol (a mixture of the *meso* and racemic modifications) to give *meso* and/or racemic isomers of the 4,5-dimethyl analogue (IIc) also in low yield. One of the two isomers of (IIc) crystallised, m. p. 40—40·5°, and was analysed (Table 1). The above reactions of (I) with glycols also took place with sodium hydroxide or sodium dissolved in glycols but the yields were lower than those in which potassium hydroxide was used.


(I)


(A)

The structure of compound (IIa) was assigned[1] by molecular weight determination, ultraviolet (u.v.) and infrared (i.r.) spectroscopy, and by the fact that it was hydrolysed to give 1,2,4,5,6,7,8,9-octachlorotricyclo[5,2,1,$0^{2,6}$]deca-4,8-diene-3,10-dione. The same conclusion as to structure of (IIa) was recently reported by Lemal

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[1] The preliminary Communication, W.-H. Chang, *Chem. and Ind.*, 1964, 709, is considered to be 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. 2,607,102/1954 (*Chem. Abs.*, 1955, **49**, 14956).

TABLE 1

Tetrachloro-1,3-dioxolan-2-spirocyclopenta-2′,4′-dienes (II)

Compound	Yield * (%)	Formula	Required (%) C	H	Cl	Found (%) C	H	Cl	B. p./(mm.)	M. p.	λ (mμ) (ε) †	$\mu_{max.}$ ‡
(IIa)	90	$C_7H_4Cl_4O_2$	32·0	1·55	54·15	31·95	1·65	54·0	78—80°/0·13	64·5—65·5°	max. 313(2390) min. 261(320)	6·19s 6·29w
(IIb)	62·5	$C_8H_6Cl_4O_2$	34·8	2·2	51·4	34·8	2·3	51·4	69/0·04	—	max. 313(1330) min. 261(290)	6·19s 6·29w
(IIc)	36	$C_9H_8Cl_4O_2$	37·25	2·8	48·9	37·85	3·05	48·5	60—100/0·1	40—40·5	max. 312(1880) min. 264(508)	6·18s 6·29w
(V)	Low	$C_9H_8Cl_4O_2$	(Analysed as the dimer)						80—90/0·09	—	(Not determined)	6·21s 6·32w
(IV)	80	$C_7H_6Cl_4O_2$							114—120/11	31 §	max. 308(2340) min. 263(575)	6·21s 6·32w

* Some isolated as the dimer. † In propan-2-ol. ‡ The absorption at 6·20 μ is about 4 times as strong as that at about 6·30 μ. § Lit.,[6] m. p. 27—28°.

TABLE 2

1,2,4,5,6,7,8,9-Octachloro-3,3:10,10-bisalkylenedioxytricyclo[5,2,1,0^{2,6}]deca-4,8-dienes

Compound	Yield	Formula	Required (%) C	H	Cl	Found (%) C	H	Cl	B. p./mm.	M. p.	$\mu_{max.}$ *
(IIIa)	Good	$C_{14}H_{18}Cl_8O_2$	32·0	1·55	54·15	31·95	1·6	54·2	160°//0·01 †	279°	6·10s, 6·24s
(IIIb)	Good	$C_{16}H_{12}Cl_8O_4$	34·8	2·2	51·4	34·9	2·6	51·45	200—204/0·10	—	6·10s, 6·24s
(IIIc)	Good	$C_{18}H_{16}Cl_8O_4$	37·25	2·8	48·9	36·8	2·35	49·85	200—220/0·10	192—194	6·10s, 6·24s
(VII)	Good	$C_{18}H_{16}Cl_8O_4$	37·25	2·8	48·9	37·35	2·8	49·4	160/0·3 †	158·5—161	6·10s, 6·21s

* Infrared absorption at 6·24 μ slightly stronger than that at 6·10 μ. † Sublimed.

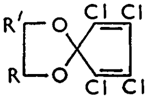
TABLE 3

2,3-Disubstituted 1,2,3,4-tetrachloro-7,7-ethylenedioxybicyclo[2,2,1]hept-5-enes

Compound	Yield (%)	Formula	Required (%) C	H	Cl	Found (%) C	H	Cl	M. p.
(VIIIa)	77	$C_{11}H_{12}Cl_4O_4$	37·75	3·45	40·5	38·0	3·75	40·6	145—147°
(VIIIb)	85	$C_{10}H_{10}Cl_4O_3$	37·45	3·15	44·3	37·7	3·55	44·3	86·5—87·5
(VIIIc)	77	$C_{13}H_{12}Cl_4O_6$	38·45	3·0	34·95	38·45	3·0	34·9	137—138
(VIIId)	40	$C_{12}H_{13}Cl_4NO_2$ *	43·75	3·65	39·75	43·6	4·25	40·2	—
(VIIIe)	47	$C_{11}H_{10}Cl_4O_4$	37·95	2·9	40·75	38·05	2·9	41·3	61·5—62·5
(IX)	91	$C_{11}H_6Cl_4O_5$	36·7	1·7	39·4	36·8	2·0	39·15	203—206
(X)	55	$C_{13}H_{14}Cl_4O_5$	39·85	3·6	36·2	40·0	3·25	36·4	188—190
(XI)	82	$C_{16}H_{12}Cl_4O_2$	50·85	3·2	37·5	50·85	3·2	37·65	115—116
(XII)	35	$C_{12}H_{10}Cl_4O_2$	43·95	3·75	43·25	43·8	3·2	43·25	80—81
(XIII)	93·5	$C_{13}H_8Cl_4O_4$	42·2	2·2	38·35	41·85	2·3	38·4	193—195
(XIV)	83	$C_{15}H_{17}Cl_4O_2$	48·55	4·6	38·25	49·2	4·4	38·4	111—112
(XV)	47	$C_{15}H_{17}Cl_4O_2$	48·55	4·6	38·25	48·6	4·4	38·45	61—64
(XVI)	32	$C_{19}H_{22}Cl_4O_2$	53·8	5·25	34·45	53·15	5·05	34·35	—

* Found: N, 3·8. Required, N, 3·9%.

et al.[7] The structures of (IIb and c) are based upon comparison of their physical constants with those of compound (IIa), analyses, the method of preparation, and the ease of dimerisation. Pure (IId and e) were not isolated but their presence was shown by u.v. and i.r. spectroscopy as well as by the method of preparation and the ease of dimerisation.



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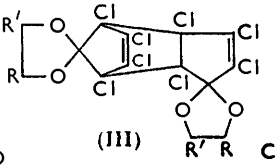
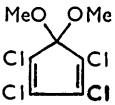
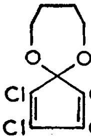


(III)

a : R = R′ = H
b : R = H, R′ = Me
c : R = R′ = Me
d : R = H, R′ = CH₂OH
e : R = H, R′=[CH₂]₄·OH



(IV)



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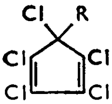

(VI) a : R = Et,
b : R = CH₂·CH:CH₂

Compounds (IIa, b, and c) all dimerised within a few hours at above 100° without a catalyst. In the liquid state, in solution, or molten, they dimerised slowly even at 25° in a few weeks, but pure crystalline (IIb and c) were stable for 3 years at 25°.

The dimers (III) (Table 2) were heated to 250° without noticeable decomposition. However, at 310°/15 mm. compound (IIIa) decomposed to give the monomer (IIa). The reversibility of the dimerisation further supported the assigned structure.

Compound (IIa) dimerised in Diels–Alder fashion to give 1,2,4,5,6,7,8,9-octachloro-3,3:10,10-bisethylenedioxytricyclo[5,2,1,$0^{2,6}$]deca-4,8-diene (IIIa) in good yield. Since only one compound was isolated, this suggested that mainly only one isomer was formed during dimerisation. By analogy,[8] the product must have an *endo*-structure, and this was confirmed by Scherer.[9] The dimer (IIIb) from (IIb) was a distillable oil (Table 2). Since theory predicts 2^4 or 16 possible stereoisomeric *endo*-isomers, no attempt was made to resolve the product. Similarly, compound (IIc) gave the related 3,3:10,10-bis-(1,2-dimethylethylenedioxy)-analogue (IIIc). Since the starting material was crystalline, implying either a pure *meso* or pure racemic compound, product (IIIc) might be one of four isomers. The distilled product was separated into two fractions, one crystalline and one liquid, but both gave the correct analysis, indicating isomers. Compounds (I) and (IV), however, did not dimerise.

The compound believed to be 2′,3′,4′,5′-tetrachloro-1,3-dioxepan-2-spirocyclopenta-2′,4′-diene (V) also dimerised. This was a liquid (Table 1) isolated as a minor by-product from the reaction of (I) with a solution from sodium dissolved in butan-1,4-diol, and changed on standing for a year into a crystalline solid with properties in accord with the dimeric structure (VII) based on analysis, molecular weight, i.r. and u.v. spectra, boiling point [much higher than that of (IIc)], and the method of preparation. It should be noted that compound (VII) can have only one *endo*-geometric isomer.

The reaction of (I) with potassium hydroxide and pinacol differed from its behaviour with other simple glycols, no characterisable product being obtained. With glycerol and potassium hydroxide, it gave an uncrystallisable and undistillable product, but the fact that the product became viscous on heating at 100° and lost its original u.v. absorption at 310 mμ suggested that the spirononadiene (IId) was obtained * and subsequently dimerised

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* The main by-product of the reaction is probably 2,3,4,5-tetrachloro-1,1-bis-(2,3-hydroxypropoxy)-cyclopentadiene because reaction of excess of propane-1,3-diol with potassium hydroxide and hexachlorocyclopentadiene gave mainly 2,3,4,5-tetrachloro-1,1-bis-(3-hydroxypropoxy)cyclopentadiene.[2] Although acetaldehyde is reported [10] to react with glycerol giving a mixture of 1,2- and 1,3-cyclic acetals, the analogue 2,3,4,5-tetrachloro-1,1-propylenedioxycyclopentadiene is unlikely to be a major product.

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

[7] D. M. Lemal, E. P. Gosselink and A. Ault, *Tetrahedron Letters*, 1964, 579.

[8] J. M. Martin and R. K. Hill, *Chem. Rev.*, 1942, **61**, 557.

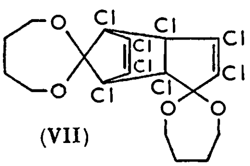
[9] K. V. Scherer, Abstract of Papers Presented at the 147th Meeting, Amer. Chem. Soc., Philadelphia, Pennsylvania, April 1964.

[10] H. Hill, A. C. Hill, and H. Gilbert, *J. Amer. Chem. Soc.*, 1928, **50**, 2242.

to (IIId). The same result as with glycerol was obtained with hexane-1,2,6-triol, *i.e.*, (IIe) was obtained and dimerised to (IIIe).

Since the assigned structure of compounds (II) and (V) contain a conjugated system and since these compounds underwent dimerisation, it was decided to study their behaviour in in the Diels–Alder reaction. If successful, this would provide support for the assigned structure both of the monomers and of the dimers. Also, it would give rise to many new compounds not otherwise easily obtainable. Compound (IIa) was selected for these experiments because it does not give geometric *endo*-isomers. The compound gave good yields of Diels–Alder adducts* with reactive dienophiles. With the less reactive dienophiles it gave lower yields of adducts because of the competing dimerisation. Since the dimer had very high meling point and low solubility in most solvents, it was usually easy to remove from the desired product by either crystallisation or distillation. Since (IIa) is a very reactive solid with a high molecular weight, is stable at room temperature when pure, has a sweet smell and does not polymerise to give a resinous product, it may be one of the ideal dienes for the preparation of derivatives of dienophiles. It gives 1 : 1 adducts with compounds containing one dienophile group, such as maleic anhydride, but-2-ene-1,4-diol, 2,5-dimethoxy-2,5-dihydrofuran, allyl alcohol, methyl maleate, indene, and vinyl acetate (Table 3), all of these adducts had i.r. absorption in the region 6·23—6·25 μ.

For dienophiles containing more than one carbon–carbon double bond, an excess of the dienophile was used to facilitate the isolation of the 1 : 1 adduct. In this way, it gave 1 : 1 adducts with cyclopentadiene, *cis,cis*-cyclo-octa-1,3-diene, *cis,cis*-cyclo-octa-1,5-diene, and cyclo-octadeca-1,5,9-triene (a mixture of isomers) (Table 3). However, when equimolar amounts of benzoquinone and (IIa) were mixed and heated, only the 1 : 1 adduct (XIII) was obtained.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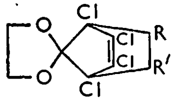
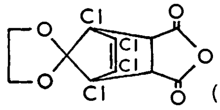

(VIII)

a : $R = R' = CH_2OH$
b : $R = CH_2{\cdot}OH,\ R' = H$
c : $R = R' = CO_2Me$
d : $R = NH{\cdot}CH_2{\cdot}CH{:}CH_2,\ R' = H$
e : $R = O{\cdot}COMe,\ R' = H$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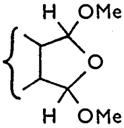
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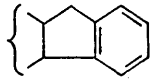
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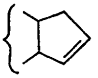
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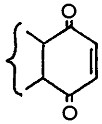
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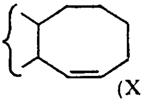
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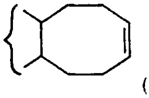
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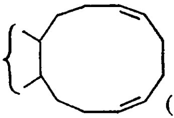
(XVI)

Whilst (I) always gave uncontrollable reaction[11] with amines during attempted Diels–Alder reactions, (IIa) reacted with diallylamine to give mainly two products. One was the expected 1 : 1 adduct (VIIId), a liquid. The other was a solid, $C_{20}H_{19}Cl_8NO_4$, m. p. 224°. The structure is believed not to be a simple 1 : 2 adduct and is being studied further.

Comparison of the relative reactivities of compounds (I), (IIa), (IV), and (VIa) toward allyl alcohol gave the order (IIa) $>$ (IV) $>$ (I) $>$ (VIa). Compound (II) reacted readily at 80°, (IV) required 115°, (I) required 140°, and (VIa) did not react during 23 hr. at 160°, but charred at 204° in a pressurised vessel.

The high reactivity of (IIa) as compared with (IV) can be easily rationalised in terms of steric effects, since the electronic effect is almost identical in this case. The dimethoxy-groups of compound (IV), with their inherent rotational freedom, offer much more steric

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* After the present work was concluded, Lemal *et al.*[7] published details of the Diels–Alder product of (IIa) with phenylacetylene. The adduct decomposed at its m. p. (127·5—128·3°) to give 2,3,4,5-tetrachlorobiphenyl, ethylene, and carbon dioxide.

[11] R. Riemschneider and B. E. Grabitz, *Monatsh.*, 1960, **91**, 22.

hindrance to an approaching dienophile than does the ethylenedioxy-group of (II), since the ethylenedioxy-group is part of a ring and therefore is denied freedom of rotation. The same reasoning was used [1] to explain that fact that (II) dimerised, whilst (IV) did not.

The higher reactivity of (I) than of (VIa) is probably due to both steric and electronic effects. Since the ethyl group is not so bulky as to disturb very much the planarity of the cyclopentadiene ring of (VIa) in the ground state, the ethyl group can only possibly block one of the two reaction sides of the cyclopentadiene ring. If only steric factors operated, one would expect (VIa) to be about half as reactive as (I). Since compound (VIa) was not reactive toward allyl alcohol even at 170°, whilst (I) reacted at 140°, the electron-donating property of the ethyl group probably plays an important role in inhibiting the reaction. This argument is consistent with the conclusion of Sauer [12] who found that (I) reacted as the electron-deficient component in the Diels–Alder reaction, *i.e.*, the Diels–Alder additions were with " inverse " electron demand. When one of the six electron-withdrawing chlorine atoms of (I) is displaced by an electron-rich group such as ethyl group, the electron deficiency of the cyclopentadiene ring is minimised, and thus compound (VIa) is not reactive toward allyl alcohol under the conditions used.

The above argument also explains the fact that (IV) is more reactive than (I) towards allyl alcohol. Both of the methoxy-groups and the chloro-groups withdraw electrons by the inductive effect and thus increase the electron deficiency and also increase the reactivity of the cyclopentadiene ring, but due to the bulkier size of the chlorine atom (which is also more rigid) than the methoxy-group,[13] (IV) is the more reactive.

The above argument also explains the fact that the ease of dimerisation of the 1,2,3,4-tetrachlorocyclopentadienes [14] are in the order 5,5-difluoro > 5,5-dihydro > 5-chloro > 5,5-dichloro.

Although allyl alcohol did not react with compound (VIa), compounds of the above type did give adducts with more reactive dienophiles, thus confirming the assumed cyclopentadiene structure.[15] 5-Allyl-1,2,3,4,5-pentachlorocyclopenta-2,4-diene (VIb) gave an adduct with maleic anhydride at 120° (but not at 80° for 23 hr.), and with styrene at 120°. A consideration of the structure based upon previous analogy [8,*] suggested that the first of these adducts was *endo*, with the allyl group *anti* to the anhydride group because an allyl group is bulkier than a chlorine atom.

EXPERIMENTAL

Analyses were by H. W. Golbraith, Knoxville, Tennessee, U.S.A. Columns for gas–liquid chromatography (g.l.c.) were $\frac{1}{4}$ in. × 2 ft. Apiezon L on Chromosorb W.

2′,3′,4′,5′-Tetrachloro-1,3-dioxolan-2-spirocyclopenta-2′,4′-diene (IIa).—Ethylene glycol (8 moles) containing potassium hydroxide (2·1 moles) was added dropwise at 25—33° (external cooling) to hexachlorocyclopentadiene (1 mole) during 45 min. The mixture was stirred until the two layers became one. After about 20 hr. the pH of the glycol solution was 8·0—8·5. Water was added to dissolve the salt and to precipitate the oily product. The oil layer was dissolved in ether and washed with saturated sodium chloride solution. After drying the organic layer and removal of solvent under diminished pressure, the residue was diluted with light petroleum (b. p. 86—100°) and cooled to −78°. Filtration gave the crude product. A portion was distilled, b. p. 78—80°/0·13 mm., and the distillate was crystallised carefully, without heating, from ether–pentane, to give the pure *spiro-compound* (IIa) (Table 1).

On heating the filtrate on a steam-bath for 18 hr. gave the dimer (IIIa) (see below) (28·5 g.), which was filtered off. Total yield of product and dimer was 262 g. (90%). Distillation of this filtrate at 0·06 mm. gave three fractions: (i) compound (I) (5·4 g.), b. p. 60—89°;

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* The Diels–Alder reaction products were assumed to give the sterically more stable products.[16]

[12] J. Sauer, D. Lang, and A. Mielert, *Angew. Chem.* (*Internat. Edn.*), 1962, **1**, 268.

[13] F. H. Westheimer in " Steric Effects in Organic Chemistry," ed. M. S. Newman, Wiley, New York, 1956, pp. 598, 643, 650.

[14] E. T. McBee *et al.*, reviewed by C. W. Roberts, *Chem. and Ind.*, 1958, 113.

[15] V. Mark, *Tetrahedron Letters*, 1961, 295.

[16] V. A. Mironov, E. B. Sobolev, and A. N. Eligarova, *Tetrahedron*, 1963, **19**, 1939.

(ii) (2·0 g.), b. p. 90—126°; (iii) (31·4 g.), b. p. 126—132°. The residue was shown to be the dimer (IIIa) by m. p. and i.r. spectroscopy. Fraction (iii) was crystallised many times from ether–pentane to give a solid, m. p. 79·5—80° [Found: C, 37·85; H, 3·2; Cl, 36·65%; *M* (osmometer), 298. Calc. for $C_9H_9Cl_3O_4$: C, 37·6; H, 3·2; Cl, 37·0%; *M*, 288].

2',3',4',5'-*Tetrachloro*-4-*methyl*-1,3-*dioxolan*-2-*spirocyclopenta*-2',4'-*diene* (IIb).—The crude product, prepared from propylene glycol (2 moles), 1,2-dimethoxyethane (300 ml., to dissolve the alkali), and potassium hydroxide (2 moles) as for compound (IIa), weighed 255 g. A portion (8·3 g.) was distilled at 80°/0·07 mm., and was identified by g.l.c. This compound tended to dimerise upon prolonged heating. It was stable at −10°, but was unstable at room temperature and dimerised completely in 1 month. The analytical sample (Table 1) had n_D^{24} 1·5440. A comparison of the extinction coefficient of this compound with other similar types of compounds (Table 1) suggested that part of the compound dimerised on standing.

2',3',4',5'-*Tetrachloro*-4,5-*dimethyl*-1,3-*dioxolan*-2-*spirocyclopenta*-2',4'-*diene* (IIc).—The crude product, similarly prepared from butane-2,3-diol (2 moles), 1,2-dimethoxyethane (300 ml., to dissolve the akali), and potassium hydroxide (2 moles) weighed 245 g. A portion (10·0 g.) was distilled to give fractions (i) (6·65 g.), b. p. 60—100°/10 mm. and (ii) (2·0 g.), b. p. 180—200°/18—30 mm. The analytical sample (Table 1) of the *dimethyl analogue* was obtained by crystallisation of fraction (i) from light petroleum (b. p. 35—60°) at −78°. Since this product was very easily dimerised, especially upon heating, the yield was calculated by g.l.c. as follows. The crude product (7 g.) was fast-distilled to give 4·48 g. of distillate, b. p. 60—100°/0·18 mm. G.l.c. indicated that it contained 66% of compound (IIc) (calculated yield, 35·4%), and three impurities, 2%, 9%, and 27%, which were not further studied.

2',3',4',5'-*Tetrachloro*-1,3-*dioxepan*-2-*spirocyclopenta*-2',4'-*diene* (V) *and its Dimer* (VII).—Butane-1,4-diol (720·0 g., 8·0 moles) was heated to 85° and metallic sodium (46·0 g., 2·0 moles) was added until a homogeneous solution was obtained. The solution was cooled, a mixture of hexachlorocyclopentadiene (272·0 g., 1·0 mole) in butane-1,4-diol (200 ml.) was added dropwise at 33—40° with external cooling, and the resulting mixture was stirred at room temperature for 3·5 days. The product was very acidic. Water was added to precipitate an oil which was added to chloroform and dilute sodium hydrogen carbonate. The organic layer was washed with water until neutral, dried, the solvent removed, and the residue distilled in small fractions to give much high-boiling material,[2] but there was also a low-boiling product (25·0 g.), b. p. 60—90°/0·065 mm. This fraction was redistilled thrice to give the *spirodioxepan* (Table 1), n_D^{25} 1·5470. After one year at room temperature about 80% of this oil solidified. It was triturated with light petroleum (b. p. 35—60°) and was filtered to give a solid which crystallised from acetone–light petroleum (b. p. 86—100°) to give the *dimer* (VII) (Table 2).

Dimer (IIIa). The monomer (IIa) (2 g.), m. p. 64·5—65·5°, was heated in an oil-bath at 120° for 2 hr. It first melted then slowly solidified. The solid was crushed, extracted with ether, and filtered to give the *dimer* (1·76 g.), which was purified by recrystallisation from chloroform several times to give the analytical sample (Table 2).

Pyrolysis of Dimer (IIIa). The dimer (5 g.) was heated at 15 mm. (pot temp. 310—320°) to give a distillate (5 g.) mainly compound (IIa), as judged by i.r. spectroscopy and by g.l.c.

Dimer (IIIb).—Monomer (IIb) (5 g.) was heated on a steam-bath for 3 hr. to give a hard resinous *product*, b. p. 200—204°/0·12 mm. (Table 2). This dimer was also obtained by keeping compound (IIb) at room temperature for 2 months.

Dimer (IIIc).—Compound (IIc) (5 g.) was heated for 5 hr. in a test-tube on a steam-bath to give a hard resin which was distilled to give the analytical sample of the *dimer*, b. p. 200—220°/0·10 mm. The product was triturated with ether. An insoluble solid was removed and recrystallised from chloroform–light petroleum, m. p. 192—194° (Table 2).

Hydrolysis of Compound (IIa).—The spiro-compound (11 g.) was heated with sulphuric acid (40 ml.) on a steam-bath for 30 min. After cooling, the mixture was poured into ice–water and filtered to give 9·5 g. of solid, m. p. 145—154° (decomp.). The solid showed an infrared spectrum which was identical with that of 1,2,4,5,6,7,8,9-octachlorotricyclo[5,2,1,$0^{2,6}$]deca-4,8-diene-3,10-dione prepared by the acid hydrolysis of 2,3,4,5-tetrachloro-1,1-dimethoxycyclopenta-2,4-diene. The above product (1 g.) was heated in water on a steam-bath for 1·5 hr. The yellow product was crystallised from acetone to give a product (0·6 g.), m. p. 145—146°. This was proved to be perchloroindenone by mixed melting point.

2,3,4,5-*Tetrachloro*-1,1,-*dimethoxycyclopenta*-2,4-*diene* (IV).—The following procedure gave a purer product and a better yield than that reported.[6] Hexachlorocyclopentadiene (1·638 g., 6·0 moles) and potassium hydroxide (911·5 g., 12·3 moles; 85% purity) were added slowly to methanol (2 l.) at 31—37° (external cooling). The mixture was kept at 30—35° for 7 hr. then at room temperature overnight. The product was slightly basic (0·5 ml. needed 0·012 m. equiv. KOH to neutralise). The product was washed with water several times until neutral. It was then added to methanol (500 ml.) and cooled in a bath at −78°. The solid obtained by filtration was distilled, b. p. 114—120°/11 mm. (960 g.), pure by g.l.c., m. p. 31° (lit.,[6] 27—28°). The filtrate was also distilled, b. p. 106—132°/11 mm. (430 g.), g.l.c. indicated 85% purity, undistillable residue, 52·0 g.

1,4,5,6-*Tetrachloro*-7,7-*ethylenedioxybicyclo*[2,2,1]*hept*-5-*ene*-2,3-*dicarboxylic Anhydride* (IX).—Maleic anhydride (0·98 g., 0·01 mole) was mixed with the spiro-compound (IIa) (2·62 g., 0·01 mole) in benzene (10 ml.). There was no evolution of heat. The solution was refluxed for 1 hr. and filtered to remove a trace of solid. The crystals which separated on cooling were collected (3·30 g.). Recrystallisation from benzene gave the *anhydride* (IX), m. p. 203—206° (Table 3).

1,2,3,4-*Tetrachloro*-7,7-*ethylenedioxy*-5,6-*dihydroxymethylbicyclo*[2,2,1]*hept*-2-*ene* (VIIIa).—A solution of the spiro-compound (IIa) (26·4 g., 0·10 mole) and but-2-ene-1,4-diol (18·0 g., 0·20 mole) in 1,2-dimethoxyethane (40 ml.) and acetone (20 ml.) was kept at room temperature for 5 days. The solvent was removed *in vacuo* and the residue (43·9 g.) distilled to give but-2-ene-1,4-diol (8·0 g.), b. p. 110°/0·10 mm., compound (VIIIa) (26·9 g., 76·5%), b. p. 210—215°/0·10—0·20 mm., and the dimer (IIIa) (1·3 g.). Two recrystallisations of the high-boiling product from ether–hexane gave the pure *dihydroxymethyl compound* (23·4 g.) (Table 3).

1,2,3,4-*Tetrachloro*-7,7-*ethylenedioxy*-5-endo-*hydroxymethylbicyclo*[2,2,1]*hept*-2-*ene* (VIIIb).—The spiro-compound (IIa) (100 g., 0·38 mole) was added to allyl alcohol (22·0 g., 0·38 mole) and 1,2-dimethoxyethane (40 ml.). Reaction was very exothermic at 80° and caused the solution to boil. The mixture was kept at 91—93° for 10 hr. Upon cooling, 11·5 g. of compound (IId) precipitated. The resulting filtrate was distilled to give the product (96·3 g.), b. p. 127—135°/0·04—0·06 mm. Recrystallisation from ether–light petroleum gave the *hydroxymethyl compound* (93·0 g., 84·5%) (Table 3).

Dimethyl 1,4,5,6-*Tetrachloro*-7,7-*ethylenedioxybicyclo*[2,2,1]*hept*-5-*ene*-2,3-*dicarboxylate* (VIIIc).—A solution of compound (IIa) (13·0 g., 0·49 mole) methyl maleate (8·60 g., 0·060 mole), and toluene (25 ml.) was kept at 25° for one day, then heated at 100° for 5 hr. Solvent was removed and the residue (15·3 g., 77·0%) was recrystallised thrice from acetone–hexane to give the *diester* (Table 3).

5-*Allylamino*-1,2,3,4-*tetrachloro*-7,7-*ethylenedioxybicyclo*[2,2,1]*hept*-2-*ene* (VIIId).—A solution from the spiro-compound (IIa) (13·0 g.) diallylamine (5·80 g.), and toluene (30 ml.) was heated as in the preceding experiment. No solid separated on keeping the product at 20° for 4 days. The solvent was removed by a stream of air, and the residue (4·2 g.) gave a product (4·0 g., 33·5%), m. p. 224° (from acetone–hexane) (Found: C, 38·35; H, 3·0; Cl, 45·9; N, 2·3. Calc. for $C_{20}H_{19}Cl_8NO_4$: C, 38·7; H, 3·25; Cl, 45·75; N, 2·25%).

The filtrate was distilled and the fraction (7·0 g., 40%), b. p. 128—140°/0·02 mm.), filtered to remove 0·20 g. of a solid and redistilled to give the *allylamine* (50%), b. p. 140—142°/0·02 mm.), n_D^{26} 1·5358 (Table 3).

1,2,3,4-*Tetrachloro*-10,10-*ethylenedioxy*-4a,9a-*dihydro*-1,4-*methanofluorene* (XI).—This was prepared as for the diester (VIIIc), using indene instead of methyl maleate. The solvent was removed and the *product* (Table 3) (15·0 g., 82·0%), recrystallised from acetone–hexane, was found to have two crystalline forms, m. p. 119—121 and 115—116°. They gave different i.r. spectra in Nujol mull but identical spectra in chloroform.

4,5,6,7-*Tetrachloro*-10,10-*ethylenedioxy*-3a,7a-*dihydro*-1,4-*methanoindene* (XII).—A mixture of the spiro-compound (IIa) (15·0 g.) cyclopentadiene (5·0 g.) and benzene (30 ml.) was kept at room temperature for 4 days and then heated on a steam-bath for 16 hr. The solvent was partly removed by evaporation and the mixture filtered to remove the dimer (IIIa) (4·6 g.). The filtrate was distilled to give a fraction, b. p. 118°/0·06 mm. This product (8·0 g.) was very soluble in hydrocarbon solvents. Many crystallisations from ether–methanol gave the pure *indene* (6·0 g., 35·3%) (Table 3).

1,2,3,4-*Tetrachloro*-9,9-*ethylenedioxy*-4a,5,8,8a-*tetrahydro*-1,4-*methanonaphthalene*-5,8-*dione* (XIII).—A mixture of the spiro-compound (IIa) (26·6 g., 0·10 mole), benzoquinone (10·8 g., 0·10 mole), and toluene (30 ml.) was heated on a steam-bath for 12·5 hr. Solid precipitated after about 2 hr. After cooling, the product was filtered off and crystallised from acetone

(20·7 g.). From the filtrate a further 14·6 g. was isolated (total yield 93·5%). The analytical sample was obtained by sublimation of the recrystallised *product* at 190°/0·01 mm.) and crystallisation from benzene (Table 3).

1,2,3,4 -*Tetrachloro* - 11,11 - *ethylenedioxy* - 4a,7,8,9,10,10a - *hexahydro* - 1,4 - *methanobenzocyclooctene* (XIV).—A solution of the spiro-compound (IIa) (37·0 g., 0·14 mole), *cis,cis*-cyclo-octa-1,3-diene (76·0 g., 0·70 mole), and benzene (125 ml.) was refluxed (94°) for 6 hr. The solvent was removed *in vacuo* on a steam-bath. The residue was distilled and the distillate (43·0 g., 83·0%), b. p. 156—168°/0·08 mm.) solidified on cooling; 60 g. was not distillable. Recrystallation several times from ether–heptane gave the *product* (Table 3).

1,2,3,4 - *Tetrachloro* - 11,11 - *ethylenedioxy* - 4a,5,6,9,10,10a - *hexahydro* - 1,4 - *methanobenzocyclooctane* (XV).—This was prepared as above using 0·15 mole of compound (IIa), and 0·75 mole of *cis,cis*-cyclo-octa-1,5-diene instead of the 1,3-diene. A white solid, precipitated upon cooling the mixture, was collected by filtration and shown to be the dimer (IIIa) (8·5 g.). The filtrate was evaporated to dryness to give the adduct (26·0 g., 45%), b. p. 152—174°/0·12—15 mm. and residue (9·0 g.). G.l.c. indicated this distillate was almost pure product. This was repeatedly crystallised from ether–hexane to give the pure *product* (Table 3).

1,2,3,4 - *Tetrachloro*-15,15-*ethylenedioxy* - 4a,5,6,9,10,13,14,14a - *octahydro* - 1,4 - *methanobenzocyclodecene* (XVI).—A solution of the spiro-compound (IIa) (39·3 g.), cyclododeca-1,5,9-triene (121·5 g.) (a mixture of isomers) and benzene (125 ml.) was refluxed for 6 hr. (94°). The solvent and the low-boiling starting materials were removed by vacuum distillation and the residue was distilled to give the product (28·8 g.), b. p. 200—220°/0·2—0·3 mm.). The pot residue was 22·2 g. The distillate was extracted with ether, giving the dimer (IIIa) (5·0 g.). The filtrate was again distilled to give a glassy *product* (20·3 g., 31·9%), b. p. 180°/0·18—0·20 mm. (Table 3).

1,4,5,6-*Tetrachloro*-7,7-*ethylenedioxybicyclo*[2,2,1]*hept*-5-*en*-2-*yl Acetate* (VIIIe).—A mixture of the spiro-compound (IIa) (39·3 g.), vinyl acetate (12·9 g.), and benzene (125 ml.) was refluxed (initial temperature 83°) for 6 hr. The solvent was removed and the product distilled. This gave a fraction (36·2 g.), b. p. 80—120°/0·25—0·20 mm. The pot residue gave the dimer (IIIa) (7·0 g.). The distillate was crystallised from ether–heptane several times to give the *ester* (24·5 g., 47·5%) (Table 3).

1,4,5,6-*Tetrachloro*-7,7-*ethylenedioxybicyclo*[2,2,1]*hept*-5-*en*-2-*ylmethyl Methacrylate*.—A mixture of the hydroxymethyl compound (VIIIb) (9·60 g., 0·03 mole), methacrylic acid (5·40 g., 0·062 mole), phenothiazine (0·20 g.), sulphuric acid (0·186 g.) and benzene (100 ml.) was refluxed for 4 hr. whilst water was removed from the condensate. After cooling, the product was washed with 5% sodium carbonate. The water-insoluble layer was dissolved in ether and was washed twice with water. The solvent was removed by evaporation *in vacuo* and the residue was distilled, b. p. 140°/0·025 mm. (10·2 g., 87·7%). The *ester* was redistilled, b. p. 140°/0·025 mm., $n_{\rm D}^{23\cdot5}$ 1·5322 (Found: C, 44·0; H, 3·6; Cl, 36·65. $C_{14}H_{14}Cl_4O_4$ requires C, 43·3; H, 3·65; Cl, 36·55%).

5-*Allylpentachlorocyclopentadiene* (VIb).—Into a refluxing mixture (45°) of hexachlorocyclopentadiene (273 g., 1·0 mole) and pentane (200 ml.) was added dropwise, triallyl phosphite (202·0 g., 1 mole) during 2 hr. The mixture was then refluxed for 2 hr. After cooling, water was added to the product, and the oil layer was washed with water several times until neutral. The product (262·5 g., 93·5%) was distilled at 60°/0·2 mm., $n_{\rm D}^{25\cdot5}$ 1·5448 (lit.,[15] b. p. 63°/0·48 mm., $n_{\rm D}^{25}$ 1·5450).

7-*Allyl*-1,4,5,6,7-*pentachlorobicyclo*[2,2,1]*hept*-5-*ene*-2,3-*dicarboxylic Anhydride*.—A mixture of maleic anhydride (20 g.), compound (VIb) (20 g.), and toluene (10 ml.) was heated slowly to 130° and maintained at this temperature for 5 hr. Two-thirds of the product was distilled to give a fraction (17·5 g., 82·8%), b. p. 180°/0·15 mm., which was crystallised from ether–light petroleum to give the *anhydride*, m. p. 118·5—119·5° (Found: C, 38·4; H, 1·9; Cl, 47·0. $C_{12}H_7Cl_5O_3$ requires C, 38·3; H, 1·9; Cl, 47·1%). Reaction at 80° for 23 hr. gave no product.

7-*Allyl*-1,2,3,4,7 - *pentachloro*-5-*phenylbicyclo*[2,2,1]*hept* - 2 - *ene*.—Prepared as above using styrene (20 g.) instead of maleic anhydride, the product was distilled twice to give the *phenyl compound* (10·7 g., 38·7%), b. p. 140°/0·05 mm. (Found: C, 49·7; H, 3·55; Cl, 46·55. $C_{16}H_{14}Cl_5$ requires C, 50·1; H, 3·7; Cl, 46·2%).

The author thanks Dr. R. Dowbenko for discussion, Dr. R. M. Christenson for encouragement, and Professor C. D. Hurd for reading the manuscript.

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[*Received*, *July* 6*th*. 1964.]