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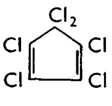
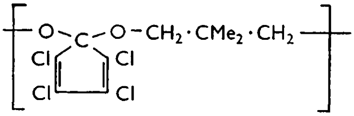
# **856.** *Hexachlorocyclopentadiene. Part IV.*[1] *Diels–Alder Adducts of 5,5-Di(hydroxyalkoxy)-1,2,3,4-tetrachlorocyclopenta-1,3-dienes and Related Compounds*

By WEN-HSUAN CHANG

THE reaction of 1·0 mole of hexachlorocyclopentadiene (I) with dissolved sodium, sodium hydroxide, or potassium hydroxide (1·33—3·00 moles) and an excess of propane-1,3-diol, butane-1,4-diol, butane-1,3-diol, or 2,2-dimethylpropane-1,3-diol gave mainly compounds of structure (II) (Table 1), amounting to one-third to one-half of the isolated products. This reaction could be carried out by the addition of (I) to the basic solution of the diol, by the addition of the diol plus base to stirred (I), or by the addition of base to a heterogeneous mixture of (I) and a diol. The crude products prepared from sodium hydroxide or metallic sodium decomposed slowly during storage (increasing acidity) or during distillation, whilst the pure products were stable.


(I)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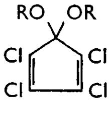
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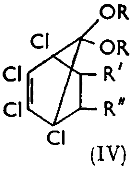
(IV)

TABLE 1

Yields and physical properties of the compounds (III)

| No. | R | Yield (%) | B. p./mm. | M. p. | $n_D$ (temp.) |
|---|---|---|---|---|---|
| 1 | $[CH_2]_3{\cdot}OH$ | 63·5 (crude) | 176—180°/0·15 | 64·5—66° | — |
| 2 | $[CH_2]_4{\cdot}OH$ | 31·8 | 186/0·035 | — | 1·5278 (25°) |
| 3 | $[CH_2]_2{\cdot}CHMe{\cdot}OH$ | 36—41 | 170/0·06 | — | 1·5219 (24) |
| 4 | $[CH_2]_2{\cdot}O{\cdot}[CH_2]_2{\cdot}OH$ | 28·5 (crude) | — | — | 1·5350 (26) |
| 5 | $CH_2{\cdot}CEt(CH_2{\cdot}OH)_2$ | 80 (crude) | — | — | — |
| 6 | $CH_2{\cdot}CMe_2{\cdot}CH_2{\cdot}OH$ | 48·3 | 160/0·03 | 56·5 | — |
| 7 | $[CH_2]_3{\cdot}OAc$ | Good | 170/0·12 | 35 | — |
| 8 | $[CH_2]_4{\cdot}OAc$ | Good | 146/0·35 | — | 1·4965 (26) |
| 9 | $[CH_2]_2{\cdot}CHMe{\cdot}OAc$ | Good | 146/0·035 | — | 1·4934 (28) |
| 10 | $CH_2{\cdot}CMe_2{\cdot}CH_2{\cdot}OAc$ | Good | 160/0·035 | 73—74 | — |

| | Found (%) | | | | Required (%) | | | U.v. spectrum (mμ) in $Pr^iOH$ (ε) | |
|---|---|---|---|---|---|---|---|---|---|
| No. | C | H | Cl | Formula | C | H | Cl | Max. | Min. |
| 1 | 37·55 | 4·1 | 40·45 | $C_{11}H_{14}Cl_4O_4$ | 37·55 | 4·0 | 40·3 | 306 (2585) | 263 (652) |
| 2 | 40·4 | 5·0 | 39·5 | $C_{13}H_{18}Cl_4O_4$ | 41·1 | 4·75 | 37·3 | 304 (2450) | 266 (882) |
| 3 | 41·05 | 4·8 | 38·25 | $C_{13}H_{18}Cl_4O_4$ * | 41·1 | 4·75 | 37·3 | 305 (2770) | 264 (760) |
| 4 | (OH value 107·8) | | 36·5 | $C_{13}H_{18}Cl_4O_6$ | (OH value 136) | | 34·4 | 308 (2025) | 273 (980) |
| 5 | (OH value 400) | | 32·4 | $C_{17}H_{26}Cl_4O_6$ | (OH value 400) | | 32·9 | 307 (2400) | 266 (736) |
| 6 | 44·35 | 5·7 | 35·55 | $C_{15}H_{22}Cl_4O_4$ | 44·15 | 5·45 | 34·75 | 306 (2110) | 266 (658) |
| 7 | 41·75 | 4·05 | 33·25 | $C_{16}H_{20}Cl_4O_6$ | 41·3 | 4·15 | 32·55 | 306 (2480) | 362 (697) |
| 8 | 43·95 | 4·8 | 30·4 | $C_{17}H_{22}Cl_4O_6$ | 44·0 | 4·8 | 30·55 | 307 (2280) | 266 (715) |
| 9 | 44·05 | 4·7 | 30·95 | $C_{17}H_{22}Cl_4O_6$ | 44·0 | 4·8 | 30·55 | 307 (2240) | 265 (701) |
| 10 | 47·05 | 5·35 | 28·45 | $C_{20}H_{28}Cl_4O_6$ | 46·35 | 5·3 | 28·8 | 306 (2220) | 204 (510) |

* OH value: Found, 276; Reqd., 296.

Some of the diols and their acetates listed in Table 1 were placed in reaction with such dienophiles as styrene, benzoquinone, ethyl acrylate, cyclopentadiene, cyclopentene, and

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[1] W.-H. Chang, (*a*) Part I, *Chem. and Ind.*, 1964, 709; (*b*) Part II, *ibid.*, p. 1491; (*c*) Part III, *J.*, 1965, 2305; (*d*) Part V, *J.*, 1965, in the press.

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*N*-phenylmaleimide, to give good yields of Diels–Alder adducts * (Table 2). However, since compounds 3 and 9 may exist in *meso* and racemic forms, their products also included the stereoisomers. The isolated crystalline solid of 13 and 18 must be one of the two possible forms, either *meso* or racemic.

TABLE 2

Preparation and physical properties of the compounds (IV)

| | | | Reactants | | Reaction conditions | | |
|---|---|---|---|---|---|---|---|
| No. | R | R′, R″ | Diene (moles) | Dienophile (moles) | Solvent | Temp. | Time (hr.) |
| 11 | $[CH_2]_2\cdot CHMe\cdot OH$ | H, Ph | 3 (0·032) | Styrene (0·144) | Benzene (200 ml.) | Reflux | 40 |
| 12 | $[CH_2]_2\cdot CHMe\cdot OAc$ | H, Ph | 9 (0·022) | Styrene (0·096) | Benzene (60 ml.) | Reflux | 40 |
| 13 | $[CH_2]_2\cdot CHMe\cdot OH$ | $CO\cdot CH{:}CH\cdot CO$ | 3 (0·100) | Benzoquinone (0·100) | Toluene (14 ml.) | Steam-bath | 14 |
| 14 | $[CH_2]_3\cdot OH$ | $CO\cdot CH{:}CH\cdot CO$ | 2 (0·100) * | Benzoquinone (0·100) | Toluene (10 ml.) | 70° | 14 |
| 15 | $[CH_2]_2\cdot CHMe\cdot OH$ | H, $CO_2Et$ | 3 (0·032) | Ethyl acrylate (0·153) | Benzene (200 ml.) | Reflux | 40 |
| 16 | $[CH_2]_2\cdot CHMe\cdot OAc$ | $CH_2\cdot CH{:}CH$ | 9 (0·042) | Cyclopentadiene (0·075) | Benzene (20 ml.) | 25°<br>Steam-bath | 96<br>16 |
| 17 | $[CH_2]_4\cdot OAc$ | $CH_2\cdot CH{:}CH$ | 8 (0·042) | Cyclopentadiene (0·075) | Benzene (20 ml.) | 25°<br>Steam-bath | 96<br>16 |
| 18 | $[CH_2]_2\cdot CHMe\cdot OH$ | $CH_2\cdot CH{:}CH$ | 3 (0·42) | Cyclopentadiene (0·075) | Benzene (20 ml.) | 25°<br>Steam-bath | 96<br>16 |
| 19 | $[CH_2]_2\cdot CHMe\cdot OH$ | $[CH_2]_6$ | 3 (0·030) | Cyclo-octene (0·39) | — | Reflux | 10 |
| 20 | $[CH_2]_3\cdot OAc$ | $CO\cdot NPh\cdot CO$ | 7 (0·00122) | *N*-Phenylmaleimide (0·00289) | Xylene (10 ml.) | Reflux | 22·5 |

* Crude.

| | | | Yield | *n* | Found (%) | | | | Required (%) | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| No. | B. p./mm. | M. p. | (%) | (temp.) | C | H | Cl | Formula | C | H | Cl |
| 11 | 205—215°/ 0·05—0·07 | — | 82·3 | Resin | 51·4 | 5·3 | 30·1 | $C_{21}H_{26}Cl_4O_4$ | 52·1 | 5·3 | 29·3 |
| 12 | 200—202/ 0·05 | — | 100 | Resin | 52·3 | 5·5 | 24·65 | $C_{25}H_{36}Cl_4O_8$ | 52·3 | 6·3 | 24·7 |
| 13 | — | 165·5—167·5 [a] | 87·0 [e] | — | 46·75 | 4·9 | 29·15 | $C_{19}H_{22}Cl_8O_6$ | 46·7 | 4·5 | 29·1 |
| 14 | — | 122—123 [b] | 44·0 [e] | — | 47·05 | 4·55 | 28·7 | $C_{19}H_{22}Cl_4O_6$ | 46·7 | 9·5 | 29·1 |
| 15 | 210/0·12— 0·14 | — | 82·8 [f] | 1·4944 (24·5°) | 44·95 | 5·2 | 29·95 | $C_{18}H_{26}Cl_4O_6$ | 45·0 | 5·5 | 29·5 |
| 16 | 200—210/ 0·25 | — | 93·8 [f] | 1·5050 (24°) | 49·9 | 5·2 | 26·7 | $C_{22}H_{27}Cl_4O_6$ | 50·0 | 5·1 | 26·8 |
| 17 | 210—212/ 0·10 | — | 72·8 [f] | 1·5095 (24·5°) | 49·0 | 5·2 | 25·75 | $C_{22}H_{27}Cl_4O_6$ | 50·0 | 5·1 | 26·8 |
| 18 | 188/0·065 | 76—77 [c] | 72·3 [f] | — | 48·3 | 5·2 | 32·1 | $C_{18}H_{24}Cl_4O_4$ | 48·4 | 5·4 | 31·8 |
| 19 | — | 116 [b] | 73·2 | — | 51·5 | 6·45 | 29·15 | $C_{21}H_{32}Cl_4O_4$ | 51·4 | 6·6 | 29·0 |
| 20 | — | 110—112 [d] | 68·4 | — | 49·1 | 4·3 | 23·6 | $C_{25}H_{25}Cl_4NO_8$ [g] | 49·3 | 4·1 | 23·2 |

[a] From acetone. [b] From acetone–hexane. [c] From benzene–pentane. [d] From benzene–hexane. [e] Calc. from crude 1. [f] Mixture of isomers. [g] N: Found, 2·1; Reqd., 2·3%.

In order to prove the presence of two hydroxyl groups in adduct 19, it was acetylated and the diacetate (21) was obtained. The acetylation of 14, however, gave a tetra-acetate (22) because the two ketone groups enolised and aromatised during the acetylation.

When equimolar parts of (I) and 2,2-dimethylpropane-1,3-diol (in 1,2-dimethoxyethane)

* Whilst the successful Diels–Alder reaction products are listed in Table 2, some other reactions were attempted without success. Thus, 3 was unreactive towards methyl methacrylate in refluxing toluene or benzene for 40—50 hr., and also towards cyclohexene at 140° for 6 hr., but at 175° for 15 min. in a pressurised vessel it gave a tar. This is surprising, especially since (I) had been reported [2] to give 88% of the adduct with cyclohexene. Also, 3 did give 73% of an adduct with cyclo-octene (Table 2).

[2] E. K. Fields, *J. Amer. Chem. Soc.*, 1954, **76**, 2709.

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were treated with potassium hydroxide, the product obtained was a polyacetal with the probable repeating unit (II). It gave adducts with maleic anhydride, allyl alcohol, methyl fumarate, and methyl maleate. The extent of the Diels–Alder reaction was determined by the disappearance of the ultraviolet absorption at 306 mμ (the disappearance of the conjugated double bonds). The bulky groups of the polymer retard the Diels–Alder reaction, and under the experimental conditions tested the following results were obtained. Completion of the reaction with maleic anhydride as dienophile in refluxing xylene for 1·5 hr.; 59—64% completion with methyl maleate at 140—155° for 4·5 hr.; 63% with allyl alcohol at 125° for 2 hr.; 48% with methyl fumarate at 140—155° for 5 hr.

*Experimental.—Compounds* 3, 4, *and* 5. A homogeneous solution of the polyol and a base was added dropwise to (I). The mixture was stirred as shown in the following Table. The products were processed.

| | (I) (moles) | Polyols (moles) | Base (moles) | Temp. (addition) | Temp. (stirring) |
|---|---|---|---|---|---|
| 3 | 0·75 | 5·5 | Na (1·0) | 32—45° | 45° (63 hr.) |
| 4 | 1·0 | 6·0 | KOH (3·0) | 44—47 | 25 (16 hr.) |
| 5 | 0·5 | 5·0 | KOH (1·0) | 65—70 | 65—70 (17 hr.) |

*Compound* 3 *from butane*-1,3-*diol.* The reaction product (very acidic) was filtered. Half of the filtrate was dissolved in ether, washed with 10% sodium carbonate and water, dried at 0·05 mm., and distilled, to give a distillate (211 g.) which was redistilled to give three fractions: (1) 21·0 g., 2 phases, b. p. 58—70°/0·8—0·1 mm., was a mixture of the two starting materials; (2) 22·0 g., b. p. 70—170°/0·08—0·05 mm., of which about half was compound 3; (3) 55·8 g., b. p. 170°/0·06 mm., $n_D^{24}$ 1·5219 (36%). The other half of the product was added to potassium hydroxide (0·50 mole) and stirred at 23° for 24 hr., to give compound 3 (41%), which, with iodine, sodium hydroxide, and dioxan, gave iodoform.

*Compound* 4 *from diethylene glycol.* Half of the product (neutral) was filtered, and the filtrate was extracted twice with ether. Evaporation of the ether layer gave compound 4 (29·5 g.).

*Compound* 5 *from* 1,1,1-*trishydroxymethylpropane.* Hexane (1 l.) was added to the reaction product to extract the unreacted (I). The bottom layer was dissolved in ether and washed with water. Removal of the ether gave compound 5 (190·5 g.) as a hard resin.

*Compounds* 1 *and* 6. Base (2 moles) (for 1, sodium hydroxide; for 6, potassium hydroxide) was added in portions to a heterogeneous mixture (for 1, 10·0 moles of propane-1,3-diol, 1·00 mole of (I); for 6, 7·0 moles of 2,2-dimethylpropane-1,3-diol, 1·00 mole of (I), 500 ml. of 1,2-dimethoxyethane) at 23—33°. The mixture was stirred overnight at 25°, and water was added to precipitate the product as an oil which was dissolved in ether and washed with water. Then, for compound 1, solvent was removed to give 488 g. of crude 1, which became strongly acidic on standing. Part of the product was distilled, b. p. 180°/0·15 mm. The product from the redistillation (b. p. 178—180°/0·15 mm.) solidified on standing, m. p. 50—59°. Recrystallisation from ether–hexane gave pure compound 1. For compound 6, part (1/42) of the product was distilled to give 4·8 g. (48·3%). The distilled product (b. p. 160°/0·03 mm.) solidified and was recrystallised twice from hexane.

*Compound* 2. A solution of sodium (2·00 moles) and butane-1,4-diol (8·0 moles) was added dropwise to (I) (1 mole) at 33°. The mixture was stirred for 3 days, to the strongly acidic product was added water (1 l.) and chloroform (1 l.), and the organic layer was washed with 10% sodium carbonate solution and water, and dried at 0·5 mm. for 5 hr., to give crude 2 (220 g., 52%). A sample (40·0 g.) was distilled, to give 25·0 g., b. p. 200—204°/0·07 mm., $n_D^{25}$ 1·5245. This was redistilled to give compound 2.

*Compounds* 7, 8, 9, *and* 10. A mixture of the appropriate diol, excess of acetic anhydride, and sodium acetate (1·0 g.) was heated at 100° for 2 hr. The product was washed with sodium carbonate solution and water, dried, distilled, and recrystallised from pentane at −78°.

*Acid hydrolysis of compound* 3. A mixture of compound 3 (22·0 g.) and concentrated sulphuric acid (150 ml.) was stirred on a steam-bath for 10 min. The temperature rose to 70°. This hot solution was poured on to ice and filtered. The filter cake was dissolved in ether, washed with water, and rinsed with hexane. Filtration yielded tetrachloropentadienone dimer (11·2 g.), m. p. 155° (decomp.), having the correct infrared spectrum.

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The crude product (m. p. 155°) (1 g.) was added to water (50 ml.) and heated on a steam-bath for 1·5 hr. The yellow product was filtered off and recrystallised from acetone, to give perchloroindenone (0·60 g.), m. p. 145—146°.

*Preparation of compounds* 11—20. A mixture of the reactants was heated as described in Table 2. The product was purified by crystallisation, distillation, or a combination of both as shown in Table 2.

9,10,11,12-*Tetrachlorotricyclo*[6,4,0,$1^{9,12}$]*tridec*-10-*en*-13-*one di*-(3-*acetoxybutyl*) *acetal* (21). This was prepared in the same way as compounds 7—10, except that 19 was the starting material. The *product* had b. p. 190—200°/0·035 mm., $n_D^{28}$ 1·5028 (Found: C, 52·05; H, 6·5; Cl, 24·6. $C_{25}H_{36}Cl_4O_6$ requires C, 52·25; H, 6·3; Cl, 24·7%).

1,2,3,4-*Tetrachloro*-9,9-*di*-(4-*acetoxybutoxy*)-1,4-*dihydro*-1,4-*methanonaphthalene*-5,8-*diol diacetate* (22). A mixture of compound 14 (20 g.), acetic anhydride (50 ml.), and anhydrous sodium acetate (1·0 g.) was heated on a steam-bath for 4 hr. Volatile substances were removed *in vacuo* on a steam-bath. To the residue was added ether, and the mixture was washed thrice with water. Hexane was added in small portions, and the dark resinous material which formed was filtered off through Celite repeatedly. The product was crystallised from methanol and cooled to −78° to give the *diacetate* (15 g.), m. p. 83—83·5° (Found: C, 49·65; H, 4·95; Cl, 21·85. $C_{27}H_{32}Cl_4O_{10}$ requires C, 49·3; H, 4·9; Cl, 21·5).

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