1316. *The Reactions of Hexachlorocyclopentadiene with Some Ether-alcohols*

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Hexachlorocyclopentadiene reacts with 3-ethyl-3-hydroxymethyloxacyclobutane and with tetrahydrofurfuryl alcohol, in the presence of alkali. The products each contain five chlorine atoms per molecule, and can undergo Diels–Alder reactions with various dienophils. Two isomeric dienes were obtained from the oxacyclobutane derivative.

HEXACHLOROCYCLOPENTADIENE (I) reacts with alcohols or thiols in the presence of alkali-metal hydroxides, forming ketals or thioketals of tetrachlorocyclopentadienone.[1,2] Allyl alcohol, however, yields 3,6,7,8,9-pentachloro-1-oxaspiro[4,4]nona-6,8-diene (II).[3] Secondary amines usually react with hexachlorocyclopentadiene to form the corresponding

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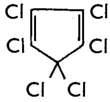
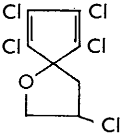
[1] J. A. Krynitsky and R. W. Bost, *J. Amer. Chem. Soc.*, 1947, **69**, 1918; J. S. Newcomer and E. T. McBee, *ibid.*, 1949, **71**, 946; J. W. Dawson and W. J. Croxall, U.S.P. 2,562,893/1951 (*Chem. Abs.*, 1952, **46**, 1587); E. P. Ordas, U.S.P. 2,697,103/1954 (*Chem. Abs.*, 1955, **49**, 15,956); Wen-Hsuan Chang, *Chem. and Ind.*, 1964, 709, 1491; *J.*, 1965, 2305; K. V. Scherer, *Abstrs.*, 147*th Amer. Chem. Soc. Mtng.*, 1964, 48N.

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

[3] Velsicol Corp., U.S.P. 2,989,543/1961 and 2,918,479/1959.

aminals;[4] however, diethanolamine yields 4-β-hydroxyethyl-6,7,8,9-tetrachloro-1-oxa-4-azaspiro[4,4]nona-6,8-diene (III).[5]


(I)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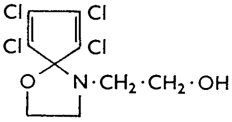

(III)

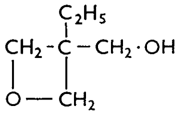
Hitherto, hexachlorocyclopentadiene has only once been reported as reacting with an alcohol to form a monoalkoxypentachlorocyclopentadiene; such a product was obtained from 2-ethylhexanol.[6] We have now found that 3-ethyl-3-hydroxymethyloxacyclobutane (IV) [7] reacts with hexachlorocyclopentadiene in the presence of potassium hydroxide, to form *two* isomers ($C_{11}H_{11}Cl_5O_2$). Tetrahydrofurfuryl alcohol appeared to react similarly; only one product ($C_{10}H_9Cl_5O_2$) could be isolated in this case. This material, however, is believed to be a mixture of isomers. Significant infrared absorption bands of these and related compounds are tabulated.

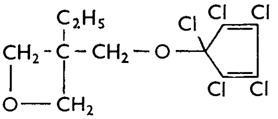
Infrared absorption maxima in the 1580—1660 cm.$^{-1}$ region

Compound	Approximate absorption frequencies (cm.$^{-1}$)		
$C_{11}H_{11}Cl_5O_2$, major product	1580	1610	
$C_{11}H_{11}Cl_5O_2$, minor product		1610	1645
$C_{10}H_9Cl_5O_2$	1580	1610	1645
Hexachlorocyclopentadiene *	1587	1621	
5,5-Dimethoxytetrachlorocyclopentadiene *	1582	1613	
1,5,5-Trimethoxytrichlorocyclopentadiene *		1613	1653

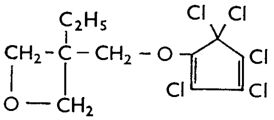
* Calculated from the values given (in microns) by McBee *et al.*[2]

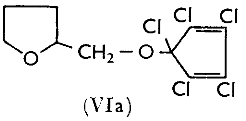
On the basis of these spectra and the evidence of McBee *et al.*[2] that reactions of methoxide ion with hexachlorocyclopentadiene and with tetrachlorocyclopentadienone dimethyl ketal occur at vinylic positions, the structure (Va) has been assigned to the major product from the oxetan (IV).

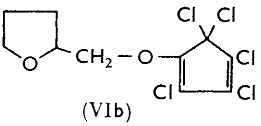

(IV)


(Va)

The isomeric product reacted readily with methanol, in the presence of an acidic catalyst. In this case, methanol both added to the unsaturated ring and opened the oxetan ring: the major product (Va) in contrast only underwent ring-opening of the oxetan cycle. From the evidence of these reactions and the infrared spectrum, we have tentatively assigned the vinyl ether structure (Vb) to this by-product, a very small amount only of which was isolated.


(Vb)


(VIa)


(VIb)

The product isolated from tetrahydrofurfuryl alcohol is believed to be a mixture of compounds having the analogous structures (VIa) and (VIb). This belief is supported by the infrared spectrum (see above) and the fact that the product, when allowed to react with acidified methanol, gave a new material, whose infrared spectrum showed absorption

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

[5] M. R. Kamal and J. E. Wicklatz, *Canad. J. Chem.*, 1964, **42**, 1500.

[6] H. Rakoff, U.S.P. 2,946,674/1960.

[7] D. B. Pattison, *J. Amer. Chem. Soc.*, 1957, **79**, 3455.

maxima at *ca.* 1620 and 1580 cm.$^{-1}$. The absorption band originally present at 1645 cm.$^{-1}$ (presumably that of a vinyl ether) completely disappeared.

The tetrahydrofurfuryl alcohol product ($C_{10}H_9Cl_5O_2$) also undergoes Diels–Alder reaction with maleic anhydride, to give a 1 : 1 adduct ($C_{14}H_{11}O_5Cl_5$) of unsharp melting point.

The reaction of hexachlorocyclopentadiene with methanol in the presence of alkali was studied in detail by McBee and his co-workers.[2] These authors were unable to isolate any monomethoxy-derivatives; they considered that a second chlorine atom was displaced in a fast step, " immeasurable by comparison with " the displacement of a first chlorine atom. The results obtained by Rakoff [6] with 2-ethylhexanol and by us with cyclic ether-alcohols can be attributed to steric effects consequent upon the large bulk of entering species.

Both the major product (Va) from 3-ethyl-3-hydroxymethyl-1-oxacyclobutane (IV) and the product from tetrahydrofurfuryl alcohol were able to undergo Diels–Alder reactions with various dienophils. The oxetan (Va) gave crystalline derivatives with the olefins used, whereas the tetrahydrofuran derivative gave products which (with the exception of the maleic anhydride adduct mentioned above) were liquid and which decomposed on attempted distillation—presumably because of reversal of the Diels–Alder reaction. Thus, the adduct with dimethyl maleate gave dimethyl fumarate on heating.

The products (Va and Vb) containing oxetan groups are of interest as their Diels–Alder adducts can be polymerised to flame-retardant materials having heavily chlorine-substituted bicyclo [2,2,1]hept-2-ene units. Synthetic resins containing similar units, and obtained by Diels–Alder reaction of perchlorocyclopentadiene derivatives with unsaturated epoxides, have been described by Porret and Leumann.[8]

EXPERIMENTAL

Reaction of Hexachlorocyclopentadiene with 3-*Ethyl*-3-*hydroxymethyloxacyclobutane.*—A mixture of hexachlorocyclopentadiene (273 g., 1 mole) and the hydroxy-oxetan [7] (116 g., 1 mole) was stirred at 10°, and potassium hydroxide (84 g.) was added (as a 50% aqueous solution) during 30 min. The mixture was stirred for a further 90 min. at 10°, and then for an additional 21 hr. at room temperature, and was then extracted with light petroleum. The solvent was evaporated from the extract, and the residue was distilled. After a fore-run of unchanged hexachlorocyclopentadiene (97 g.), the main product was obtained as a fraction of b. p. 122—126°/0·2 mm. (139 g.).* The distilled product was recrystallised from light petroleum at $-40°$ to give white crystals (88 g.) of the " major " isomer, m. p. 40·5° (Found: C, 37·4; H, 3·4; Cl, 50·6. $C_{11}H_{11}Cl_5O_2$ requires C, 37·45; H, 3·15; Cl, 50·4%).

The mother-liquors from the crystallisation were evaporated and a sample of the residue introduced on to a column of alumina, which was then eluted with a mixture of petroleum and benzene. The first compound eluted was the isomeric " minor " product (Found: C, 37·72; H, 3·1; Cl, 49·5%). This process was repeated several times in order to obtain sufficient quantities of pure isomer for examination.

The two isomeric products (1 g.) were each treated with methanol (50 ml.) and toluene-*p*-sulphonic acid (0·1 g.). After the mixtures had been left overnight, the infrared spectra of both products showed a substantial reduction in the intensity of the band at 980 cm.$^{-1}$ (oxetan) but no appreciable change in the 1600—1650 cm.$^{-1}$ region. When the mixtures were refluxed for 6 hr., a substantial decrease in the bands at 1610 and 1645 cm.$^{-1}$ was noticed for the " minor " product but not for the " major " product.

Reaction of Hexachlorocyclopentadiene with Tetrahydrofurfuryl Alcohol.—A mixture of hexachlorocyclopentadiene (273 g.) and tetrahydrofurfuryl alcohol (120 g.) was stirred and cooled, while solid potassium hydroxide (84 g.) was added during 4 hr., the temperature being kept below 35° during addition. The mixture was then stirred at room temperature for 16 hr. Light petroleum was added, and the mixture filtered. Carbon dioxide was passed through the filtrate to neutralise any remaining alkali, and the solution was again filtered. Removal of

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* It is important that the temperature of the contents of the flask should preferably not exceed 200° during distillation, as sudden exothermic decomposition is likely to occur above this temperature.

[8] D. Porret and E. Leumann, *Chimia*, 1962, **16**, 72; CIBA, B.P. 870,958/1961.

solvent and distillation of the residue gave starting materials (131 g.) and a higher-boiling fraction (117 g.) of product, which was purified by redistillation (b. p. 134—135°/0·7 mm., n_D^{20}, 1·5472) (Found: C, 35·7; H, 2·8; Cl, 52·35; O, 9·1. $C_{10}H_9Cl_5O_2$ requires C, 35·5; H, 2·7; Cl, 52·4; O, 9·45%).

This material (1 g.) was refluxed for 4 hr. with methanol (50 ml.) and toluene-*p*-sulphonic acid (0·1 g.). The product then showed infrared absorption bands at *ca.* 1620 and 1580 cm.$^{-1}$ in contrast to the starting material which had three absorption maxima at 1580, 1610, and 1645 cm.$^{-1}$.

Diels–Alder Reactions of the "Major" Oxetan Product.—(a) *With dimethyl maleate.* A mixture of the oxetan (35·49 g.), dimethyl maleate (14·4 g.), and xylene (250 ml.) was heated under reflux for 16 hr. When the mixture was cooled in an ice–salt mixture, the adduct (32 g., m. p. 139—140°) separated (Found: C, 41·5; H, 4·1; Cl, 35·8%. $C_{18}H_{19}Cl_5O_6$ requires C, 41·1; H, 3·9; Cl, 35·85%).

(b) *With cyclopentadiene.* The oxetan (35·3 g.) and freshly-prepared cyclopentadiene (40 g.) were mixed; an exothermic reaction occurred. Removal of dicyclopentadiene *in vacuo* gave a semi-crystalline mass, from which the adduct (23 g., m. p. 83·5—87°) was obtained by recrystallisation from light petroleum. Recrystallisation once more from petroleum gave pure material, m. p. 87—88° (Found: C, 46·0; H, 4·2; Cl, 42·5. $C_{16}H_{17}Cl_5O_2$ requires C, 45·9; H, 4·1; Cl, 42·35%).

(c) *With maleic anhydride.* A mixture of the oxetan (17·7 g.), purified maleic anhydride (4·9 g.), and dry benzene (150 ml.) was heated under reflux for 16 hr. The solvent was removed under reduced pressure; the residual pale yellow crystals were recrystallised from chloroform, yielding the adduct (7 g.), m. p. 215° (Found: C, 39·85; H, 3·2; Cl, 39·5; O, 17·8. $C_{15}H_{13}Cl_5O_2$ requires C, 40·0; H, 2·9; Cl, 39·35; O, 17·8%).

(d) *With bicyclo*[2,2,1]*hepta*-2,5-*diene.* A mixture of the oxetan (35·3 g.), bicycloheptadiene (11 g.), and xylene (125 ml.) was boiled under reflux for 6 hr. When the mixture was cooled crystals (2 g.) separated; these had m. p. 300—310° after recrystallisation from chloroform. Analysis showed that this material was the 2 : 1-adduct (Found: C, 43·8; H, 3·8; Cl, 44·4. $C_{29}H_{30}Cl_{10}O_4$ requires C, 43·7; H, 3·8; Cl, 44·5%). When this experiment was repeated with a large excess of bicycloheptadiene (25 g. with 7 g. of the oxetan derivative), the 1 : 1-adduct (m. p. 139°) was obtained (Found: C, 48·9; H, 4·4; Cl, 39·8; O, 7·3. $C_{18}H_{19}Cl_5O_2$ requires C, 48·6; H, 4·3; Cl, 39·9; O, 7·2%).

Reactions of the Tetrahydrofurfuryl Derivative with Dienophils.—(a) *With cyclopentadiene.* The tetrahydrofurfuryl derivative (16·9 g.) and freshly-prepared cyclopentadiene (30 g.) were mixed; the mixture became warm, and was heated under reflux for 4 hr. Removal of volatile materials *in vacuo* gave a residual oil, which decomposed on attempted distillation.

(b) *With dimethyl maleate.* The chlorine-containing diene was treated similarly with an equimolar amount of dimethyl maleate. An oil was obtained which yielded only dimethyl fumarate on attempted vacuum distillation.

(c) *With maleic anhydride.* A mixture of the chlorine-containing diene (16·9 g., 0·05 mole), maleic anhydride (4·9 g., 0·05 mole), and benzene (100 ml.) was refluxed for 16 hr. After removal of benzene the resulting oil partially crystallised. Recrystallisation from benzene–light petroleum mixture yielded crystals having m. p. 115—129°. Recrystallisation yielded material (m. p. 127—140°) which analysed satisfactorily for a 1 : 1 adduct (Found: C, 38·3; H, 2·5; O, 18·6; Cl, 40·4%. $C_{14}H_{11}O_5Cl_5$ requires C, 38·5; H, 2·5; O, 18·3; Cl, 40·6%).

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