Table II. Tetrachloroethyl Thiolsulfonates, $RSO_2SCHClCCl_3$[a]

| R | M.P., °C. | Infrared Absorption ($SO_2$) Cm.$^{-1}$ [c,d] | | NMR[b] | | Calculated Formulas | Carbon, % | | Hydrogen, % | | Chlorine, % | | Sulfur, % | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Phenyl | CHCl | | Calcd. | Found | Calcd. | Found | Calcd. | Found | Calcd. | Found |
|  | 89-90 | 1135[c] | 1330[d] | 2.04<br>2.38 | 4.04 | $C_8H_5Cl_5O_2S_2$ | 25.65 | 25.98<br>25.76[e] | 1.34 | 1.51<br>1.46[e] | 47.33 | 48.00<br>47.40[e] | 17.12 | 16.49<br>17.09[e] |
|  [f] | 84-86 | 1140[c] | 1338[d] | | | $C_8H_5BrCl_4O_2S_2$ | 22.93 | 23.63 | 1.20 | 1.24 | 42.31 | 40.04 | 15.30 | 15.26 |

[a] Melting points uncorrected. Analyses, except[e], by Weiler & Strauss. [b] TMS internal reference (τ values given). [c] *Sym*, S–O. [d] *Asym*, S–O. [e] Analyzed by Galbraith Laboratories, Knoxville, Tenn. [f] Not enough for NMR analysis.

analysis by NMR indicated a mixture of 85% 1,2,2,2-tetrachloroethanesulfenyl chloride and 15% of the 1,1,2,2-tetrachloroethyl isomer). Water was then added to the mixture and the light yellow organic product separated. The aliphatic compounds were diluted with ether and dried over sodium sulfate before chromatographing. The aromatic compounds, which did not crystallize from the oil, were handled similarly.

The compounds, which were purified by thin-layer chromatography, were applied in about 5% ether solution to plates coated to a thickness of 250 microns with silica gel $GF_{254}$ (Merck) containing a fluorescent indicator, and were developed in benzene, or benzene-petroleum ether (30 to 60° C.)-chloroform, 8:8:1 by volume.

The NMR data were obtained on a Varian DP-60 nuclear magnetic resonance spectrometer. Chemical shifts were determined by side bands applied with an audio-oscillator for which the frequency is continuously monitored by an electronic counter. The samples were run in a concentration of 20 to 40% by volume in carbon tetrachloride at a temperature of approximately 33° C.

The infrared spectra were obtained on a Beckman IR-4 spectrophotometer using sodium chloride optics. The liquid samples were run neat and the solids in Nujol mulls.

## LITERATURE CITED

(1) Backer, H.J., Westerhuis, E., *Rec. Trav. Chim.* **71**, 1082 (1952).

(2) Lo, C.P., Wilson, H.F., Croxall, W.J., *J. Am. Chem. Soc.* **76**, 1704 (1954).

(3) Weil, E.D., Geering, E.J., Smith, K.J., French Patent **1,276,665** (Oct. 16, 1961).

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# Synthesis of 1,2,3,4,9,9-Hexachloro-1,4,4a,5,6,7,8,8a-octahydro-1,4-methanonaphthalene-6,7-dicarboxylic Acid and Ester Derivatives

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**The reaction of 4-cyclohexene-1,2-dicarboxylic anhydride (I) with hexachlorocyclopentadiene under Diels-Alder conditions gives rise to two stereoisomeric adducts. Both isomers, II-m.p. 278–280° C. and III-m.p. 256–257.5° C., are reactive with hydroxyl compounds in the formation of mono- and diesters.**

THE CHEMISTRY of hexachlorocyclopentadiene has been reviewed (*2, 3*). Of particular interest have been the various products from the Diels-Alder reaction with unsaturated dicarboxylic acids or their anhydrides. This paper reports the Diels-Alder reaction of hexachlorocyclopentadiene with 4-cyclohexene-1,2-dicarboxylic anhydride (I).

## EXPERIMENTAL

**Preparation of Isomeric 1,2,3,4,9,9-Hexachloro-1,4,4a,5,6,7,8,8a-octahydro- 1,4-methanonaphthalene-6,7-dicarboxylic Anhydrides.** In a 3-liter, three-necked, round-bottomed resin kettle equipped with a reflux condenser, stirrer, thermometer, nitrogen inlet tube, and heating mantle (controlled with a Honeywell Brown Pyr-O-Vane) was placed 456 grams (3 moles) of *cis*-4-cyclohexene-1,2-dicarboxylic anhydride (Allied Chemical Corp.), 816 grams (3 moles) of hexachlorocyclopentadiene (Hooker Chemical Co.), and 320 grams (25% based on reactants) of mixed xylenes. The mantle temperature was maintained at 210° C., and the reaction temperature 173° C. at its highest, dropped to 159° C. during 16 hours. The reaction mixture was cooled to 110° C., treated with 300 ml. of mixed xylenes, and equilibrated at 110° C. for 4 hours; the solid product was isolated by suction filtration through a steam jacketed Büchner funnel. The filter cake was washed with two 100-ml. portions of hot (100° C.) mixed xylenes and then with two 100-ml. portions of *n*-heptane. The crude product was dried under vacuum at 110° C. for 16 hours to give 1000 grams (78.4%), m.p. 240° C., of isomeric adducts. Recrystallization from 4000 ml. of 1,2-dibromoethane gave 791 grams (62%) of a high melting isomer (compound II), m.p. 278° C. Distillation of the filtrate to a volume of 500 ml. gave 150 grams (11.8%) of a mixture of high and low melting isomers. Repeated recrystallization of this mixture of isomers from toluene-butanone resulted in the isolation of the pure low melting material (compound III), m.p. 256–

257.5° C. (Melting points were capillary and corrected.) Anal. Calcd. for $C_{13}H_8Cl_6O_3$ (II): C, 36.74; H, 1.89; Cl, 50.06. Found: C, 36.84; H, 1.37; Cl, 50.10. Anal. Calcd. for $C_{13}H_8Cl_6O_3$ (III): C, 36.74; H, 1.89; Cl, 50.06; molecular weight, 424.95. Found: C, 36.57; H, 1.83; Cl, 50.04; molecular weight (benzene) 424.2.

The homogeneity of compound III was determined on a F&M Model 300 programmed temperature gas chromatograph (F&M Scientific Corp., Wilmington, Del.). The chromatograph was set for manual operation, column temperature 275° C., injection port temperature 305° C., attenuation set at 1, powerstat 51, and 180 ma. current. The column was 0.25-inch thin-walled stainless steel tubing, 3 feet long packed with 20% silicone gum rubber on 42- to 60-mesh firebrick. Sample size was 6 ml. of a 45% by weight solution in acetone. Injection of pure II gave no peak for III, and the injection of more III gave no peak for II.

**Preparation of 1,2,3,4,9,9-Hexachloro-1,4,4a,5,6,7,8,8a-octahydro-1,4-methanonaphthalene-6,7-dicarboxylic Acids.** In a 1-liter, single-necked, round-bottomed flask was placed 42.4 grams (0.1 mole) of the isomeric 1,2,3,4,9,9-hexachloro-1,4,4a,5,6,7,8,8a-octahydro-1,4-methanonaphthalene-6,7-dicarboxylic anhydride, 16 grams (0.4 mole) of sodium hydroxide, and 400 ml. of deionized water. The mixture was warmed on the steam bath for 4 hours; the warm clear solution was filtered, cooled, and made acid (pH 2 to 3) by the addition of sulfuric acid. The white crystalline precipitate was collected on a suction filter, washed with deionized water, and dried under vacuum at 60° C. for 16 hours to yield 42 grams (96%) of the isomeric 1,2,3,4,9,9-hexachloro-1,4,4a,5,6,6,8,8a-octahydro-1,4,-methanonaphthalene-6,7-dicarboxylic acid. The anhydride, m.p. 278° C., on mixture was an equivalent of the acid, m.p. 274° C., gave a m.p. 260° to 274° C. The anhydride, m.p. 256–257.5° C. gave an acid with a m.p. of 252° C. Infrared spectra of each of the acids showed no anhydride peaks, and neutral equivalents confirmed the presence of two acid groups.

Typical syntheses of ester derivatives of II and III are given for the sake of completeness. It was advantageous in certain experiments to effect conversion of the anhydride to the acid in situ before esterification.

**Preparation of the Dimethyl Ester of Compound II.** In a 1-liter, single-necked, round-bottomed flask equipped with a reflux condenser protected with a Drierite tube, a gas inlet tube, and cooled in an ice bath, was placed 42.4 grams (0.1 mole) of compound II, 1.8 grams (0.1 mole) of water, and 500 ml. of anhydrous methanol containing 0.05 gram of *p*-toluenesulfonic acid. The mixture was transferred to a steam bath and heated under reflux for 2 hours, the cooled mixture was immersed in an ice bath, and dry hydrogen chloride was bubbled through the mixture for 20 minutes. The resulting mixture was let stand at room temperature for 3 hours, poured over 1 kg. of ice, and filtered. The solid was dissolved in 500 ml. of benzene, washed with a 5% aqueous solution of sodium bicarbonate and water, treated with anhydrous magnesium sulfate, filtered, and evaporated to dryness under reduced pressure at 60° C. The resulting solid was recrystallized from *n*-heptane to give 42 grams (98%) of product, m.p. 102–103° C. (Table I).

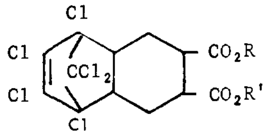
**Preparation of the Dimethyl Ester of Compound III.** In a 75-ml., single-necked, round-bottomed flask equipped with a reflux condenser protected with a Drierite tube and cooled in an ice bath, was placed 4.25 grams (0.01 mole) of 1,2,3,4,9,9-hexachloro-1,4,4a,5,6,7,8,8a-octahydro-1,4-methanonaphthalene-6,7-dicarboxylic anhydride (compound III) and 25 ml. of anhydrous methanol. The mixture was transferred to a steam bath and heated under reflux for 6 hours, the cooled mixture was immersed in an ice bath, and anhydrous hydrogen chloride was bubbled through the mixture for 45 minutes. The resulting mixture was let stand at room temperature for 16 hours, poured over 50 grams of ice, and filtered. A solution of the solid in 50 ml. of benzene was washed with a 5% aqueous solution of sodium bicarbonate and with water, dried over anhydrous magnesium sulfate, filtered, and evaporated to dryness under reduced pressure at 60° C. The semisolid residue was recrystallized from *n*-heptane to give 3.61 grams (85%) of needle-like crystals, m.p. 132° C. Anal. Calcd. for $C_{15}H_{14}Cl_6O_4$: C, 38.25; H, 2.99; Cl, 45.16. Found: C, 38.28; H, 3.30; Cl, 44.75.

Preparations of the esters described in Table I were run in a similar fashion. In the case of the diallyl and half methallyl esters of II, *tert*-butyl catechol (0.5 gram) was added to inhibit polymerization during the synthesis. The dibutyl ester of III was isolated in 38% yield as a liquid, b.p. 190° C. at 0.1 mm., $n_D^{25}$ 1.5190, $d_4^{25}$ 1.3533. Anal. Calcd. for $C_{21}H_{26}Cl_6O_4$: C, 45.54; H, 4.83; Cl, 38.27; MR, 125.09. Found: C, 45.77; H, 4.37; Cl, 38.70; MR, 124.61.

## DISCUSSION

The authors discovered that the reaction of hexachlorocyclopentadiene with 4-cyclohexene-1,2-dicarboxylic anhydride proceeds readily under more severe conditions

Table I. Esters Derived from the Isomeric 1,2,3,4,9,9-Hexachloro-1,4,4a,5,6,7,8,8a-octahydro-1,4-methanonaphthalene-6,4-dicarboxylic Anhydride (Compound II)



| Substituents |  | Yield, | M.P., |  | Composition, % |  |  |  |  |  |
|---|---|---|---|---|---|---|---|---|---|---|
|  |  |  |  |  | Carbon |  | Hydrogen |  | Chlorine |  |
| R | R′ | % | ° C. | Formula | Calcd. | Found | Calcd. | Found | Calcd. | Found |
| $CH_3$— | $CH_3$— | 98 | 102–103 | $C_{15}H_{14}Cl_6O_4$ | 38.24 | 37.99 | 2.99 | 3.14 | 45.16 | 44.80 |
| iso-$C_3H$— | H— | 68 | 119–120 | $C_{19}H_{22}Cl_6O_4$ | 39.62 | 39.68 | 3.33 | 3.33 | 43.86 | 43.80 |
| $C_3H_5$[a]— | $C_3H_5$[a]— | 70 | 78–79 | $C_{19}H_{18}Cl_6O_4$ | 43.62 | 43.72 | 3.46 | 3.87 | 40.66 | 40.51 |
| $C_4H_8$[b]— | H— | 68 | 124–126 | $C_{17}H_{16}Cl_6O_4$ | 41.08 | 41.17 | 3.24 | 3.24 | 42.80 | 43.00 |
| *n*-$C_4H_9$— | *n*-$C_4H_9$— | 73 | 56.57 | $C_{21}H_{26}Cl_6O_4$ | 45.54 | 45.43 | 4.83 | 4.72 | 38.27 | 38.21 |
| *n*-$C_8H_{17}$— | *n*-$C_8H_{17}$— | 47 | 33.34 | $C_{29}H_{42}Cl_6O_4$ | 52.16 | 52.01 | 6.34 | 6.21 | 31.86 | 31.60 |
| $C_8H_{17}$[c]— | $C_8H_{17}$[c]— | 75 | [d] | $C_{29}H_{42}Cl_6O_4$ | 52.16 | 52.35 | 6.34 | 6.35 | 31.86 | 31.14 |

[a] Allyl. [b] Methallyl. [c] 2-Ethylhexyl. [d] Viscous liquid, b.p. above 225° C., at 0.1 mm., $n_D^{27}$1.5051.

than are required for the reaction of hexachlorocyclopentadiene with some of the simpler conjugated dienophilic dicarboxylic acids or anhydrides (*2*, *3*). At temperatures above 150° C. in inert solvents, *m*-xylene, mixed xylenes, *o*-dichlorobenzene, or with no solvent, a Diels-Alder reaction takes place to give two isolable products. One of these, compound II, has a melting point of 278° C. and is the predominant isomer produced under the conditions of the reaction. The other isomer, compound III, has a melting point of 256–257.5° C. and is isolated in 10 to 20% yield.

The total assignment of stereochemical configurations for compounds II and III has not been possible to date. Partial assignments and hence nonidentity of compounds II and III have been made using nuclear magnetic resonance. Compounds II and III were examined along with an authentic sample of the hexachlorocyclopentadiene-cyclohexene adduct (compound IV), m.p. 76–77° C. (*1*). NMR spectra were determined in pyridine and in carbon tetrachloride with 10 p.p.m. of tetramethylsilane as an internal reference. In compound IV, the group at 7.2 and 7.3 has a width at least 10 c.p.s. The breadth and shift indicate that this is the tertiary proton trans (180° C.) to the axial proton 8.7 and 9.0, whose spread and shift are consistent. Thus the cyclohexene ring has the boat conformation. Nothing can be surmised about the position of the $CCl_2$ bridge with respect to the ring in compounds II, III, or IV (Table II).

The anhydrides were converted by standard procedures into a series of esters; half-esters were easily prepared by reaction of the anhydrides with alcohols and no catalyst. The diesters of the high melting isomer (compound II) were prepared from methyl, ethyl, allyl, *n*-butyl, 2-ethylhexyl, and *n*-octyl alcohols. Isopropyl and methallyl alcohols could only be forced to the half-ester stage.

In preparations of the dimethyl esters of II and III, the synthesis of the dimethyl ester of the low melting anhydride, compound III, gave a solid product, m.p. 132° C. This ester, m.p. 132° C., may be compared with the solid ester, m.p. 102–103° C. prepared from the higher melting anhydride, compound II. The dialkyl esters of III prepared to date are uniformly lower melting than the comparable esters of II (Table I).

Table II. Tau Value Shifts

| Compound IV in $CCl_4$ | Compound IV in Pyridine | Compound II in Pyridine | Compound III in Pyridine |
|---|---|---|---|
| ... | ... | 6.5 | 6.33[a] |
| 7.20 | 7.28 | 7.4 | 6.97[b] |
| 8.20 | 8.53 | 7.4 | 7.50 |
| 8.69 | 9.00 | 8.4 | 8.33[c] |

[a] Hydrogens alpha to the carbonyl. [b] Tertiary hydrogens. [c] Prow or stern hydrogens.

## INFRARED SPECTRA

Infrared spectra were recorded using a Beckman IR-9 spectrometer in the region 400 to 3800 cm.$^{-1}$. Solid state spectra were recorded using a mull technique, and the mulling agents used were Nujol (400 to 1333 cm.$^{-1}$) and Fluorolube (1330 to 3800 cm.$^{-1}$).

The compounds show a medium band in the 1599 to 1607 cm.$^{-1}$ region $\nu_{C=C}$ stretching. Apparently, the occurrence of $\nu_{C=C}$ at lower frequencies and increased intensity indicates substitution (chlorine) when compared with $\nu_{C=C}$ for cyclohexene, ~1650 cm.$^{-1}$. Carbon chlorine stretching consistently show up in the 675 to 875 cm.$^{-1}$ region in all of the compounds.

The carbonyl stretching frequency shows up at 1770 to 1780 cm.$^{-1}$, and the two carbonyl stretching frequencies show up at 1770 to 1780 cm.$^{-1}$ and 1700 to 1712 cm.$^{-1}$; the higher frequency band is weak, while the lower frequency band is strong. This is characteristic of the cyclic anhydride moiety.

In the esters, the $\nu_{C=O}$ at ~1750 cm.$^{-1}$ is clearly inappropriate for the anhydride or the compounds having a free carboxylic acid grouping and is correct for an ester of the $R—CO_2CH_3$ form where R— is not conjugated with the carbonyl.

A weak but definite band at 2850 cm.$^{-1}$ in the methyl ester series is characteristic of a methoxy group. A strong band at 1200 cm.$^{-1}$ is characteristic of esters of the $RCO_2R'$ form where R— is again not conjugated with the carbonyl group.

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## LITERATURE CITED

(1) Riemschneider, R., Kerstein, D., *Monatsh. Chem.* **91**, 1024 (1960).
(2) Roberts, C.W., *Chem. Ind. (London)* **1958**, p. 110.
(3) Ungnade, H.E., McBee, E.T., *Chem. Rev.* **58**, 249 (1958).

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# Improved Preparation of 2,3-Dihydro-*p*-dioxin(Dioxene)

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**2,3-Dihydro-*p*-dioxin (dioxene) was prepared in 78% yield by a liquid-phase dehydrogenation-dehydration of diethylene glycol at 230° to 250° C.**

THE COMPOUND 2,3-dihydro-*p*-dioxin (dioxene) has previously been prepared in low yield by the reaction of 2,3-dichloro-1,4-dioxane with Grignard reagents such as methyl, ethyl, or 1-butyl magnesium bromide (*4*) and by the reaction of 2,3-dichloro-1,4-dioxane with magnesium iodide (*5*). Also prepared in low yields by the catalytic vapor-phase dehydrogenation-dehydration of ethylene glycol (*3*), it is obtained in small amounts as a by-product from the copper chromite-catalyzed dehydrogenation of diethylene glycol; the major product is 2-*p*-dioxanone (*2*).

The authors were able to prepare dioxene in 78% yield by a liquid-phase dehydrogenation-dehydration of diethylene glycol at 230° to 250° C. Table I summarizes results obtained with various catalysts. Of the catalysts tested, the most effective was a copper chromite–potassium acid

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