

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

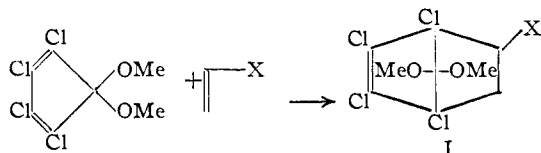
The Diels-Alder Reaction with 5,5-Dimethoxy-1,2,3,4-tetrachlorocyclopentadiene¹BY E. T. MCBEE, W. R. DIVELEY² AND J. E. BURCH³

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5,5-Dimethoxy-1,2,3,4-tetrachlorocyclopentadiene undergoes the Diels-Alder reaction with a variety of dienophiles. The adducts from acrylic acid, styrene and *p*-chlorostyrene have been hydrolyzed to the corresponding carbonyl bridge compounds which lose carbon monoxide on heating. The resulting hydroaromatic chloro compounds can be dehydrogenated in good yield.

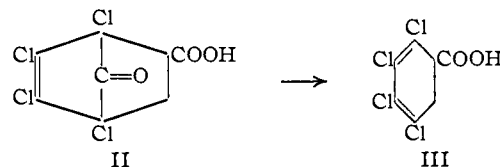
Discussion

Previous studies in this Laboratory have established that 5,5-dimethoxy-1,2,3,4-tetrachlorocyclopentadiene undergoes the Diels-Alder reaction with maleic anhydride under relatively mild conditions,⁴ as is the case with hexachlorocyclopentadiene⁵ and 1,2,3,4-tetrachlorocyclopentadiene.⁶ The Diels-Alder reaction with 5,5-dimethoxy-1,2,3,4-tetrachlorocyclopentadiene has now been extended to ten other dienophiles. The adducts I are formed in good yields in accordance with the following equation when the reactants are refluxed for 48 hours. The physical properties and analyses of the compounds appear in Table I.



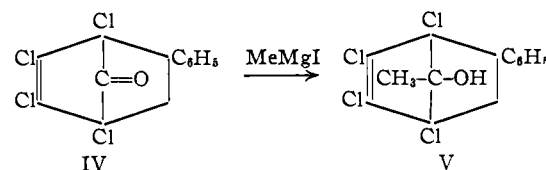
The Diels-Alder adducts with a ketal bridge are of particular interest since they permit the synthesis of aromatic systems by a sequence of reactions involving the removal of the bridge. Thus, in the case of the acrylic acid and acrylonitrile adducts (compound I, X = COOH and CN), the hydrolysis

with cold concentrated sulfuric acid gives the carbonyl bridge compound II which loses carbon monoxide on heating to 200°. The resulting 1,6-dihydro-

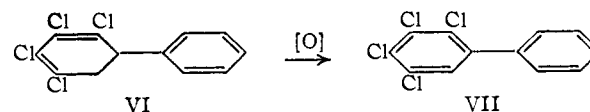


dro-2,3,4,5-tetrachlorobenzoic acid (III) has been converted to the known 2,3,4,5-tetrachlorobenzoic acid by oxidation with potassium permanganate or with chromic trioxide in acetic acid. In the latter case 1,2,3,4-tetrachlorobenzene is obtained as by-product.

The styrene adduct is similarly hydrolyzed with sulfuric acid to a cyclic ketone IV, which has been characterized by preparation of a dinitrophenylhydrazone and by reaction with methylmagnesium iodide. The resulting tertiary alcohol V can be converted to an acetate, from which it is regener-



ated on hydrolysis. The ketone IV loses carbon monoxide on refluxing with nitrobenzene to give 1,6-dihydro-2,3,4,5-tetrachlorobiphenyl (VI) which can be dehydrogenated to 2,3,4,5-tetrachlorobiphenyl (VII) by use of chromic oxide in acetic acid. The latter compound VII has also been prepared in one step by condensing 5,5-dimethoxy-1,2,3,4-tetrachlorocyclopentadiene with phenylacetylene.



2,3,4,5,4'-Pentachlorobiphenyl (VIII) has been prepared from the adduct of *p*-chlorostyrene (I, X = C₆H₄Cl) by a series of reactions analogous to those used in the conversion of the styrene adduct to 2,3,4,5-tetrachlorobiphenyl.

Experimental⁸

Starting Materials.—Hexachlorocyclopentadiene⁹ was converted to 5,5-dimethoxy-1,2,3,4-tetrachlorocyclopentadiene by the method of Newcomer and McBee.⁴ *p*-Chloro-

(7) Cf. C. F. H. Allen, *Chem. Revs.*, **37**, 309 (1945).

(8) All temperatures uncorrected.

(9) Hexachlorocyclopentadiene was generously supplied by the Hooker Electrochemical Company.

TABLE I

DIELS-ALDER ADDUCTS WITH TETRACHLORO-5,5-DIMETHOXYCYCLOPENTADIENE

Dienophile	Yield, %	M.p., °C.	Carbon		Hydrogen	
			Calcd.	Found	Calcd.	Found
Allyl alcohol ^a	71	83.5-84.5	37.29	37.28	3.75	3.80
Allyl bromide	90	63-64	31.17	31.42	2.86	2.85
Acrolein	65	Liq. ^b	37.54	37.52	3.15	3.04
Acrylic acid ^c	76	163-164	35.71	35.88	2.98	2.85
Acrylonitrile ^d	70	88-89	37.89	37.91	2.86	3.01
<i>p</i> -Benzoquinone	82	162-164	41.97	42.14	2.70	2.80
<i>p</i> -Chlorostyrene	92	101-102	44.72	44.92	3.23	3.36
Indene	52	120-121	50.53	50.78	3.68	3.78
Methyl vinyl ketone	38	86-87	39.52	39.51	3.59	3.75
Styrene	94	82-83	48.89	48.80	3.80	3.90

^a Calcd. for C₁₀H₁₂Cl₄O₄: Cl, 44.1. Found: Cl, 44.0. ^b B.p. 155-156° (5 mm.), *n*_D²⁰ 1.5292; 2,4-dinitrophenylhydrazone, m.p. 180-181°, calcd. for C₁₆H₁₄Cl₄N₄O₈: N, 11.20. Found: N, 11.40. ^c Calcd. for C₁₀H₁₀Cl₄O₄: neut. equiv., 336. Found: neut. equiv., 340. ^d Calcd. for C₁₀H₇Cl₄NO₂: N, 4.42. Found: N, 4.25. Calcd. for C₁₃H₁₀Cl₄O₄: Cl, 38.2. Found: Cl, 38.1.

(1) Presented before the Organic Section at the 121st Meeting of the American Chemical Society, Buffalo, N. Y., March 24-27, 1952.

(2) From the Ph.D. thesis of W. R. Diveley, Purdue University, 1952.

(3) From the Master's thesis of J. E. Burch, Purdue University, 1948.

(4) J. S. Newcomer and E. T. McBee, *THIS JOURNAL*, **71**, 949 (1949).

(5) E. A. Prill, *ibid.*, **69**, 82 (1947).

(6) E. T. McBee, R. K. Meyers and C. F. Baranaukas, *ibid.*, **77**, 86 (1955).

styrene was prepared by the addition of methylmagnesium iodide to *p*-chlorobenzaldehyde, then dehydrating the resulting carbinol with fused potassium bisulfate.¹⁰

Preparation of the Diels-Alder Adducts.—Equimolecular amounts of 1,2,3,4-tetrachloro-5,5-dimethoxycyclopentadiene and appropriate dienophiles were refluxed gently for 48 hours. The reaction mixtures were diluted with solvents suitable for crystallization, *viz.*, petroleum ether, ethanol, methanol or water and allowed to cool. The adduct from acrolein, which could not be induced to crystallize, was distilled twice under reduced pressure. The physical properties and analyses of the adducts are listed in Table I.

1,6-Dihydro-2,3,4,5-tetrachlorobenzoic Acid (III).—Powdered 7,7-dimethoxy-1,4,5,6-tetrachlorobicyclo[2.2.1]5-heptene-2-carboxylic acid (41.5 g., 0.124 mole) was rapidly stirred at room temperature with concentrated sulfuric acid (150 ml., sp. gr. 1.84) for 48 hours. The reaction mixture was filtered with suction. The crude product was dissolved in 600 ml. of ice-water and the solution was extracted with three 150-ml. portions of ether. The colorless product, which remained after removal of the ether, was dissolved in 5% aqueous sodium carbonate, filtered and acidified with concentrated hydrochloric acid. The ether extracts of this solution gave 32.3 g. (90%) of crude colorless 7-keto-1,4,5,6-tetrachlorobicyclo[2.2.1]5-heptene-2-carboxylic acid, m.p. 91–94°. A mixture of this acid (15.3 g., 0.0528 mole) and nitrobenzene (100 ml.) was heated at 145–155° until gas evolution ceased. The gas was identified as carbon monoxide. After cooling, the reaction mixture was extracted with three 150-ml. portions of 5% aqueous sodium bicarbonate. The combined extracts were acidified and the precipitated acid was filtered and crystallized repeatedly from methanol, colorless needles, m.p. 150–151°, yield 10.9 g. (79%).

Anal. Calcd. for $C_7H_2Cl_4O_2$: C, 32.06; H, 1.53; neut. equiv., 262. Found: C, 32.20; H, 1.58; neut. equiv., 267.

Oxidation of 1,6-dihydro-2,3,4,5-tetrachlorobenzoic acid (4 g.) with chromic anhydride (5 g.) in glacial acetic acid (50 ml.) at temperatures below 40° gave 1.3 g. (39%) of colorless, alkali-insoluble needles (from alcohol), m.p. 45–46°, identified as 1,2,3,4-tetrachlorobenzene (lit. value, m.p. 45°).¹¹

Anal. Calcd. for $C_6H_2Cl_4$: C, 33.33; H, 0.93. Found: C, 33.48; H, 0.82.

The alkali soluble portion of the oxidation products was isolated as a colorless solid, yield 1 g. (25%), m.p. 189–190°, identical with 2,3,4,5-tetrachlorobenzoic acid (literature melting point 186°).¹² This acid was the sole product when the crude 1,6-dihydro-2,3,4,5-tetrachlorobenzoic acid (m.p. 91–94°) was oxidized with potassium permanganate in acetone, m.p. and mixed m.p. 189–190°.

Anal. Calcd. for $C_7H_2Cl_4O_2$: neut. equiv., 260. Found: neut. equiv., 261.

2,3,4,5-Tetrachlorobenzoic Acid.—A solution of 24.1 g. (0.076 mole) of 7,7-dimethoxy-1,4,5,6-tetrachlorobicyclo[2.2.1]5-heptene-2-nitrile in 100 ml. of concentrated sulfuric acid was allowed to stand overnight at room temperature. A colorless solid, which separated when the mixture was poured on ice, was filtered and dried in air, m.p. 80–100°. This crude material (1.1 g.) was added in small portions to 30 ml. of boiling nitrobenzene. The solution turned dark and a gas was evolved which was identified as carbon monoxide. The solution was allowed to cool and extracted with 10% aqueous sodium bicarbonate. The organic acid was regenerated by acidification with concentrated hydrochloric acid and extracted with ether. Removal of the ether left a small amount of colorless needles, m.p. 188–190° which did not depress the melting point of the 2,3,4,5-tetrachlorobenzoic acid obtained previously.

5-Phenyl-1,2,3,4-tetrachlorobicyclo[2.2.1]2-heptene-7-one (IV).—A mixture of 10 g. of finely divided 7,7-dimethoxy-5-phenyl-1,2,3,4-tetrachlorobicyclo[2.2.1]2-heptene and 100 g. of concentrated sulfuric acid was rapidly stirred at room temperature for 48 hours. The solid phase was filtered, washed with water until free from acid and crystallized from methanol, m.p. 144–145°, yield 5.5 g. (63%).

(10) C. G. Overberger and J. H. Saunders, *Org. Syntheses*, **28**, 31 (1948).

(11) R. A. Gotts and L. Hunter, *J. Chem. Soc.*, **125**, 447 (1924).

(12) P. Tust, *Ber.*, **20**, 2439 (1887).

Anal. Calcd. for $C_{13}H_8Cl_4O$: C, 48.45; H, 2.48; Cl, 44.10. Found: C, 48.50; H, 3.08; Cl, 43.90.

The 2,4-dinitrophenylhydrazones crystallized in orange plates from ethanol, m.p. 217–218°.

Anal. Calcd. for $C_{19}H_{12}Cl_4N_4O_4$: N, 11.16. Found: N, 11.19.

1,6-Dihydro-2,3,4,5-tetrachlorobiphenyl (VI).—A solution of 5-phenyl-1,2,3,4-tetrachlorobicyclo[2.2.1]2-heptene-7-one (5 g.) in nitrobenzene (50 ml.) was heated at 200° until gas evolution ceased. The gas was identified as carbon monoxide. The reaction mixture was steam distilled to remove the nitrobenzene. The residue was allowed to cool and was filtered with suction. The crude solid was decolorized with Norit and crystallized from methanol in short prisms, m.p. 85–86°, yield 4.2 g. (93%).

Anal. Calcd. for $C_{12}H_8Cl_4$: C, 49.00; H, 2.72. Found: C, 48.98; H, 2.83.

2,3,4,5-Tetrachlorobiphenyl (VII).—Chromic anhydride (3 g.), dissolved in glacial acetic acid (25 ml.), was added in small portions to 1,6-dihydro-2,3,4,5-tetrachlorobiphenyl (5 g.) in glacial acetic acid (50 ml.) at 60°. After the initial exothermic reaction, the temperature of the mixture was maintained at 60° for one hour. The green reaction mixture was diluted with water and filtered with suction. The crude solid product was crystallized from methanol, m.p. 92–92.5°, yield 4.1 g. (82%).

Anal. Calcd. for $C_{12}H_6Cl_4$: C, 49.32; H, 2.06. Found: C, 49.34; H, 1.97.

The same compound was also obtained by the following method: Equimolar amounts (0.1 mole each) of 5,5-dimethoxy-1,2,3,4-tetrachlorocyclopentadiene and phenylacetylene were refluxed for 6 hours with benzene (50 ml.). The benzene was removed by distillation. The black residue was decolorized with Norit in a 1:1 mixture of benzene and methanol and evaporated to dryness. The dark residue was extracted with hot methanol and decolorized from the same solvent. One crystallization from methanol gave colorless needles, m.p. and mixed m.p. 89–90°, yield 4.9 g. (17%). Considerable black polymeric material remained insoluble in methanol.

5-(*p*-Chlorophenyl)-1,2,3,4-tetrachlorobicyclo[2.2.1]2-heptene-7-one.—The analogous reaction of 7,7-dimethoxy-5-(*p*-chlorophenyl)-1,2,3,4-tetrachlorobicyclo[2.2.1]2-heptene with sulfuric acid furnished 65% of the colorless ketone, m.p. 136–137° (from methanol).

Anal. Calcd. for $C_{13}H_7Cl_5O$: C, 44.72; H, 3.23. Found: C, 44.92; H, 3.36.

1,6-Dihydro-2,3,4,5,4'-pentachlorobiphenyl.—This compound was prepared analogous to 1,6-dihydro-2,3,4,5-tetrachlorobiphenyl in 90% yield. The colorless needles melted at 107.5–108.5°.

Anal. Calcd. for $C_{12}H_7Cl_5$: C, 43.84; H, 2.13. Found: C, 44.05; H, 2.30.

2,3,4,5,4'-Pentachlorobiphenyl (VIII).—Solid 1,6-dihydro-2,3,4,5,4'-pentachlorobiphenyl (1 g.) was added in small portions to a solution of chromic anhydride (1 g.) in acetic acid (25 ml.) at 80°. The reaction was complete in 1.5 hours. The mixture was poured into excess cold water and the precipitated solid was filtered and washed with water. Recrystallization from methanol gave colorless needles melting at 98–99°, yield 7.4 g. (75%).

Anal. Calcd. for $C_{12}H_5Cl_5$: C, 44.10; H, 1.53. Found: C, 43.98; H, 1.58.

7-Methyl-5-phenyl-1,2,3,4-tetrachlorobicyclo[2.2.1]2-heptene-7-ol (V).—Methylmagnesium iodide was prepared by the conventional method from 10.5 g. (0.074 mole) of methyl iodide and 1.5 g. (0.062 g. atom) of magnesium turnings. To this Grignard reagent was added dropwise a solution of 11.9 g. (0.037 mole) of 5-phenyl-1,2,3,4-tetrachlorobicyclo[2.2.1]2-heptene-7-one in a minimum amount of ether. After completed addition, the mixture was refluxed 1.5 hours. The magnesium salts were hydrolyzed by cautious addition of 100 ml. of 10% aqueous sulfuric acid, the ether layer was separated and combined with two 75-ml. ether extracts of the aqueous solution. The ether solutions were distilled to remove the solvent and the colorless residue was crystallized from petroleum ether (b.p. 60–70°), m.p. 93–94°, yield 9.6 g. (76%).

Anal. Calcd. for $C_{14}H_{11}Cl_4O$: C, 49.70; H, 3.55. Found: C, 49.72; H, 3.51.

The acetate of this alcohol (2.55 g.) was obtained by refluxing with acetyl chloride (15 ml.) for 1.5 hours and allowing the mixture to stand overnight. The reaction mixture was poured onto ice with stirring. The solid ester was filtered with suction and crystallized from petroleum ether (b.p. 30–60°), m.p. 108–110°, yield 2.1 g. (73%).

Anal. Calcd. for $C_{16}H_{14}Cl_4O_2$: C, 50.53; H, 3.69. Found: C, 50.53; H, 3.93.

The acetate was saponified by refluxing with excess 20% ethanolic potassium hydroxide for 1.5 hours. The mixture was poured into excess water and filtered with suction. The crude solid carbinol on crystallization from petroleum ether (b.p. 60–70°) gave pure 7-methyl-5-phenyl-1,2,3,4-tetrachlorobicyclo[2.2.1]heptene-7-ol which did not depress the melting point of an authentic sample.

5-Bromomethyl-1,2,3,4-tetrachlorobicyclo[2.2.1]heptene-7-one.—The cleavage of 5-bromomethyl-7,7-dimethoxy-1,2,3,4-tetrachlorobicyclo[2.2.1]heptene by means of sulfuric acid gave 68% of cyclic ketone, m.p. 108–109° (from petroleum ether, b.p. 90–100°).

Anal. Calcd. for $C_8H_8BrCl_4O$: C, 28.32; H, 1.49. Found: C, 28.32; H, 1.48.

7,7-Dimethoxy-1,4,5,6-Tetrachlorobicyclo[2.2.1]heptene-2-carboxylic Acid.—A saturated solution of potassium permanganate in acetone was added dropwise with stirring at room temperature to a solution of 3 g. of 7,7-dimethoxy-2-formyl-1,4,5,6-tetrachlorobicyclo[2.2.1]heptene, prepared from dimethoxytetrachlorocyclopentadiene and acrolein, in 50 ml. of acetone until a purple color persisted. The manganese dioxide was removed by filtration and the filtrate was evaporated. The colorless residue was crystallized from aqueous ethanol and melted at 162–163°. It did not depress the melting point of the acrylic acid adduct.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

The Synthesis and Reactions of 5,5-Difluorotetrachlorocyclopentadiene¹

By E. T. McBEE, D. K. SMITH AND H. E. UNGNADE

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The dechlorination of difluorohexachlorocyclopentene (I) with zinc and hydrochloric acid gives 5,5-difluorotetrachlorocyclopentadiene (II) which undergoes the Diels–Alder reaction with suitable dienophiles. The structure of II has been established by elimination of the CF_2 bridge in its Diels–Alder adduct with dimethyl acetylenedicarboxylate. The reactions of II compared with hexachlorocyclopentadiene are correlated with the stability of the carbon–fluorine bonds and the pronounced electronegativity of the CF_2 group.

Discussion

Numerous attempts have been made to prepare a fluorine-containing cyclopentadiene by the replacement of the doubly allylic chlorine atoms of hexachlorocyclopentadiene.^{2–4} All the results indicate that fluorine adds to one of the double bonds as readily as it exchanges with chlorine, since only polyfluoropolychlorocyclopentenes are isolated. The problem now has been approached by fluorinating octachlorocyclopentene and generating the diene system by dehalogenation.

The fluorination of octachlorocyclopentene with antimony trifluoride in the presence of antimony pentachloride proceeds in a stepwise fashion to give polychlorocyclopentenes containing from one to six fluorine atoms. Henne and Zimmerschied⁵ have established the structure of 1,2-dichlorohexafluorocyclopentene by oxidation to hexafluoroglutaric acid. They have proposed structural formulas for the other fluorination products based solely on the mode of action of the fluorinating agent employed. More recently Latif⁶ has offered alternative structures for the partially fluorinated polychlorocyclopentenes. However, his proposals are based apparently on the premise that zinc

and ethanol remove only vicinal chlorine atoms, a view which is not valid for cyclic⁷ or acyclic compounds.^{8,9}

The dechlorination of difluorohexachlorocyclopentene (I) with zinc dust and hydrochloric acid gives difluorotetrachlorocyclopentadiene (II). Dechlorination also can be effected by pyrolysis at temperatures above 480°, analogous to octachlorocyclopentene,¹⁰ or by the platinum-catalyzed hydrogenation of I, but the yields in these reactions are lower.

The difluorotetrachlorocyclopentadiene II is a colorless liquid, b.p. 45° (4 mm.). It dimerizes on standing at room temperature to a colorless, crystalline solid III, m.p. 280–281°, from which it can be regenerated by pyrolysis at 480°. This constitutes an excellent method for preparing the pure diene II, since the dimer is purified easily by recrystallization. II fails to give a test with alcoholic silver nitrate solution, being unlike hexachlorocyclopentadiene and 1,2,3,4,5-pentachlorocyclopentadiene in this respect.¹¹

Difluorotetrachlorocyclopentadiene (II) readily gives the Diels–Alder reaction with various olefinic and acetylenic dienophiles either with or without solvent. The physical properties and analyses of the adducts are listed in Table I. The adduct IV with dimethyl acetylenedicarboxylate is formed exothermically when the components are heated to

(1) This paper is based on a portion of the thesis submitted by Delmont K. Smith to the Graduate School of Purdue University in partial fulfillment of the requirements for the Ph.D. degree.

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