g. (28%) of 1,1,1,2,2-pentafluoro-3-pentanol, b.p. 97–98°, n^{20}_{D} 1.3291 (lit. b.p. 98°, n^{20}_{D} 1.3280)[17] when pentafluoropropionaldehyde was used; 34.8 g. (54%) of 2,2,3,3,4,4,4-heptafluoro-1-butanol, b.p. 93–95°, n^{20}_{D} <1.3000 and 14.8 g. (20%) of 4,4,5,5,6,6,6-heptafluoro-3-hexanol, b.p. 114–115°, n^{20}_{D} 1.3260 (lit. b.p. 113.5°, n^{20}_{D} 1.3255)[18] were obtained when heptafluorobutyraldehyde was used.

The Reaction of Ethylmagnesium Iodide with Pentafluoropropionaldehyde in Magnesium Bromide Etherate.—Magnesium bromide was prepared by slowly adding 96 g. (0.6 mole) of bromine to a well-stirred mixture of 14.6 g. (0.6 g. atom) of magnesium turnings in 300 ml. of dry ether. The aldehyde, 49 g. (0.33 mole), was distilled into this mixture through a gas inlet tube reaching above the surface of the liquid, and stirring was continued for an additional 1.5 hours. The flask was cooled in an ice-bath and approximately 0.6 mole of ethylmagnesium iodide was added dropwise over a two-hour period. Hydrolysis was carried out in the flask with 500 ml. of 15% aqueous sulfuric acid, the product was taken up in ether, dried, and the ether removed by distillation. Rectification of the residual liquid gave 7.8 g. (16%) of 2,2,3,3,3-pentafluoropropanol, b.p. 81–83°, and 30.2 g. (51%) of 1,1,1,2,2-pentafluoro-3-pentanol, b.p. 95–97°.

The Reaction of Pentafluoropropionaldehyde with Ethylmagnesium Iodide in Pyridine and in Triethylamine.—The Grignard reagent (0.6 mole) was prepared in the usual manner in ether, and filtered through glass wool with nitrogen pressure into a dry, 1-liter, three-necked flask fitted with a Dry Ice reflux condenser, an efficient stirrer and an addition funnel containing 300 ml. of freshly dried and distilled amine (pyridine or triethylamine). The ether was removed under reduced pressure and the amine was added before the removal was complete. The flask was cooled in an ice-bath, 49 g. (0.33 mole) of aldehyde was distilled in, and the mixture stirred for 1 hour. The reaction mixture was hydrolyzed in the flask by the dropwise addition of 500 ml. of 30% aqueous sulfuric acid. The solution was then made acidic with 50% aqueous sulfuric acid, extracted with ether, dried and rectified to give 10.1 g. (20%) of 1,1,1,2,2-pentafluoropropanol, b.p. 80–82°, and 23.2 g. (39%) of 1,1,1,2,2-pentafluoro-3-pentanol, b.p. 96–98° when pyridine was used. With triethylamine as a solvent the products were 28.5 g. (57%) of 1,1,1,2,2-pentafluoropropanol and 17.8 g. (30%) of 1,1,1,2,2-pentafluoro-3-pentanol.

The Reaction of Pentafluoropropionaldehyde with Ethylmagnesium Iodide in Anisole.—The Grignard reagent (0.6 mole) was prepared directly in 500 ml. of dry anisole, and filtered into a three-necked flask, cooled in an ice-bath and fitted with a Dry Ice reflux condenser and an efficient stirrer. Pentafluoropropionaldehyde (49 g., 0.33 mole) was distilled into the reaction flask, stirring was continued for an additional hour, and the mixture was hydrolyzed in the flask with 200 ml. of 10% aqueous sulfuric acid. The product was taken up in ether, dried over Drierite and rectified to give 29.1 g. (58%) of 1,1,1,2,2-pentafluoropropanol and 18.2 g. (30%) of 1,1,1,2,2-pentafluoro-3-pentanol.

The Reaction of Alkyllithium Compounds with Perfluoro Aldehydes.—The alkyllithium compounds were prepared in ether in the usual manner with excess lithium,[19] and filtered into a 1-liter, three-necked flask fitted with an efficient stirrer, a Dry Ice reflux condenser and a gas inlet tube or an addition funnel, depending on whether fluoral or heptafluorobutyraldehyde was added. Approximately two moles of organometallic compound was used to one mole of carbonyl compound, and the quantities never exceeded one mole of alkyllithium. The total reaction time varied from 4 to 12 hours at ice temperatures, and the hydrolysis was carried out in the same flask with 20% aqueous sulfuric acid. The product was worked up in the usual manner to give 18.4 g. (70%) of 1,1,1-trifluoro-2-propanol, b.p. 76–78°, n^{20}_{D} 1.3171, when methyllithium was treated with 23 g. (0.23 mole) of fluoral, and 51.7 g. (68%) of 1,1,1,2,2,3,3-heptafluoro-4-hexanol, b.p. 112–114°, n^{20}_{D} 1.3250, when ethyllithium was treated with 67 g. (0.33 mole) of heptafluorobutyraldehyde.

West Lafayette, Indiana

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[17] E. T. McBee, J. F. Higgins and O. R. Pierce, This Journal, **74**, 1387 (1952).

[18] E. T. McBee, O. R. Pierce and W. F. Marzluff, *ibid.*, **75**, 1609 (1953).

[19] H. Gilman, *et al.*, *ibid.*, **71**, 1499 (1949).

[Contribution from the Department of Chemistry, Purdue University]

1,2,3,4-Tetrachlorocyclopentadiene. I. The Preparation of the Diene and its Reaction with Aromatic Aldehydes and Dienophiles

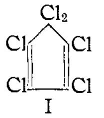
By E. T. McBee, R. K. Meyers[1] and C. F. Baranauckas[2]

Received July 16, 1954

1,2,3,4-Tetrachlorocyclopentadiene has been prepared by reduction of hexachlorocyclopentadiene with zinc dust and hydrochloric acid. The new diene reacts with aromatic aldehydes to give 1,2,3,4-tetrachloro-6-arylfulvenes. It forms adducts with maleic anhydride, cyclopentadiene and *p*-benzoquinone.

Discussion

When hexachlorocyclopentadiene (I) is reduced with zinc and absolute ethyl alcohol, cyclopentadiene can be isolated from the reaction products. Part of the chlorine is retained on reduction with stannous chloride, as is the case with zinc and hydrochloric acid. The latter reagent affects only the two allylic chlorine atoms and gives a good yield of 1,2,3,4-tetrachlorocyclopentadiene (II).



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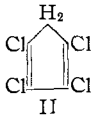

II

1,2,3,4-Tetrachlorocyclopentadiene is a colorless solid melting at 62–63°.[3] It dimerizes on heating turns dark on exposure to light and air and gives off phosgene under the influence of ozone. 1,2,3,4-Tetrachlorocyclopentadiene can be kept for several weeks at room temperature in well-filled brown bottles. With aqueous or alcoholic sodium hydroxide or with aqueous sodium carbonate, 1,2,3,4-tetrachlorocyclopentadiene rapidly gives a blue-green color which changes to black. It does not react with alcoholic silver nitrate in the cold, whereas hexachlorocyclopentadiene gives an immediate precipitate with the same reagent.

Attempts to condense II with aromatic alde-

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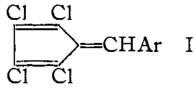
[1] In part from the Ph.D. Thesis of R K. Meyers, Purdue University, February, 1950.

[2] In part from the Ph.D. Thesis of C. F. Baranauckas, Purdue University, February, 1948.

[3] R. Riemschneider, who investigated the reduction of hexachlorocyclopentadiene with zinc and hydrochloric acid, reports a crystalline product, m.p. 62°, with the structure 1,2,3,4 tetrachloro-5-(2',3',4',5'-tetrachlorocyclopentadienyl)-cyclopentadiene [*Z. Naturforsch.*, **6B**, 463 (1951); and *Chimie and industrie*, **64**, 698 (1950)]. In view of the present work, it is considered highly probable that the compound was actually 1,2,3,4-tetrachlorocyclopentadiene.

hydes in the presence of bases were unsuccessful because of the instability of the compound toward basic reagents. However, substituted fulvenes III were prepared by refluxing alcoholic solutions of II and aromatic aldehydes. The yields, melting points and analyses of the intensely colored fulvenes which separate on cooling of the reaction mixtures are listed in Table I. The fulvenes III are stable toward air; but on oxidation with chromic acid, they are converted to the corresponding aromatic acids, *e.g.*, 1,2,3,4-tetrachloro-6-*p*-methoxyphenylfulvene is converted to *p*-methoxybenzoic acid and oxidation products of hexachlorocyclopentadiene.



III

1,2,3,4-Tetrachlorocyclopentadiene reacts with cyclopentadiene, maleic anhydride and *p*-benzoquinone under relatively mild conditions. By analogy with the adducts of hexachlorocyclopentadiene,[4] the reaction products are believed to be derivatives of [2.2.1]bicycloheptene. The cyclopentadiene adduct has been chlorinated to give both addition and substitution products, $C_{10}H_7Cl_5$ and $C_{10}H_7Cl_7$.

TABLE I

6-ARYL-1,2,3,4-TETRACHLOROFULVENES

Aryl	M.p., °C.	Yield, %	Analyses, %			
			Carbon[b]		Hydrogen	
			Calcd.	Found	Calcd.	Found
Phenyl	81–82	48	48.6[a]	48.2[a]	..	..
4-Chlorophenyl	143–144	57	54.4[a]	54.6[a]	..	..
4-Hydroxyphenyl	163–167 dec.	16	46.0[a]	45.7[a]	..	..
4-Dimethylamino-phenyl	126–127	51	50.1	50.3	3.28	3.16
4-Methoxyphenyl	127–128	50	48.4	48.4	2.54	2.48
3-Nitrophenyl	144	24	42.2[a]	42.6[a]	..	..
4-Hydroxy-3-methoxyphenyl	178–179	32	46.2	46.2	2.55	2.53
3,4-Methylenedioxyphenyl	153–154	45	46.4	46.4	1.78	1.73
3,4-Dimethoxyphenyl	138–139	47	47.8	47.7	2.60	2.84
Sytryl	144–145	41	52.8	52.5	2.52	2.48
Furyl	109–110	50	42.6	42.6	1.42	1.43

[a] Chlorine analysis. [b] Carbon and hydrogen analyses by H. Galbraith.

Experimental[5]

Reduction of Hexachlorocyclopentadiene (I) with Zinc and Ethanol.—A mixture of 136 g. of hexachlorocyclopentadiene and 100 g. of granulated zinc was heated to 60° in a 3-liter flask equipped with dropping funnel, stirrer and downward condenser. External heating was stopped and absolute ethanol (500 ml.) was added slowly during 2 hours, with cooling, so that the temperature remained below 70°. The distillate (300 ml.) was rectified from a four-foot column packed with Pyrex helices and yielded 8 g. (25%) of cyclopentadiene, b.p. 41–43°. On standing, the diene was converted to the dimer, m.p. 33°, which did not depress the melting point of an authentic sample.

1,2,3,4-Tetrachlorocyclopentadiene (II).—A solution of 273 g. of hexachlorocyclopentadiene in 100 ml. of petroleum ether (b.p. 35–37°) was added to a suspension of 13.1 g. of zinc dust in 100 ml. of water. Hydrochloric acid (600 ml. of 6 *N*) was added first slowly, then more rapidly, with stirring. The temperature of the reaction mixture did not exceed 65°. After the addition of the acid, the mixture was stirred for about 12 hours. The organic layer was separated, washed with water, cooled in an ice-bath and filtered with suction, yielding 60 g. of yellow-brown solid. The mother liquors furnished 96 g. of red-brown oil which decomposed during attempts to distil it. The solid material after three recrystallizations from acetone and three from ether was obtained as colorless prisms, m.p. 62–63°.

Anal. Calcd. for $C_5H_2Cl_4$: C, 29.46; H, 0.99; Cl, 69.6; mol. wt., 203.9. Found: C, 29.61, 29.58; H, 1.10, 1.21; Cl, 69.9, 69.5; mol. wt., 200, 204.

Improved yields of the substance were obtained by an alternate procedure: A slurry of 520 g. of zinc dust, previously treated with a cold aqueous solution of 50 g. of copper sulfate, was added with stirring to a solution of 825 g. of hexachlorocyclopentadiene in an equal volume of petroleum ether (b.p. 30–60°). Over a period of 3.5 hours, concentrated hydrochloric acid (625 ml.), diluted with an equal volume of water, was added with cooling to the resultant suspension at such a rate that the mixture gently refluxed. The reaction mixture was filtered with suction and the filtrate was separated into layers. The petroleum ether layer was cooled in an ice-bath and the crystallized solid was filtered with suction. A second crop of tan crystals separated from the mother liquor on cooling. The combined yield of crude diene was 366 g. (59%), m.p. 56–62°. Recrystallization from low-boiling petroleum ether (b.p. 35–37°) raised the melting point to 62–63°. A colorless product can also be obtained by distillation under reduced pressure, but with higher losses.

Dimer.—A solution of 60 g. (0.34 mole) of 1,2,3,4-tetrachlorocyclopentadiene in 50 ml. of benzene was refluxed on a steam-bath for 18 hours. The benzene was removed and 20 ml. of methanol was added to the residue. The crude tan dimer (35 g.) was filtered and dried. Recrystallization from nitromethane and from methanol gave 27 g. (45%) of colorless product, m.p. 190–192°.

Anal. Calcd. for $C_{10}H_4Cl_8$: C, 29.4; H, 0.99; mol. wt., 408. Found: C, 29.4; H, 1.02; mol. wt., 383, 386.

General Procedure for the Preparation of 1,2,3,4-Tetrachlorofulvenes.—A solution of 0.1 mole of 1,2,3,4-tetrachlorocyclopentadiene and 0.1 mole of an aromatic aldehyde in 50 ml. of ethanol was refluxed gently on a steam-bath. The mixture gradually turned dark and solid material separated. After 16–18 hours, the reaction mixture was cooled and the precipitate was filtered with suction. The intensely colored products were crystallized from appropriate solvents, usually ethanol.

Oxidation of 1,2,3,4-Tetrachloro-6-(*p*-methoxyphenyl)-fulvene.—Concentrated sulfuric acid (10 ml.) was added with stirring to a mixture of 2 g. of 1,2,3,4-tetrachloro-6-(*p*-methoxyphenyl)-fulvene, 10 ml. of acetic acid, 10 ml. of water and 6 g. of chromium trioxide, contained in a 250-ml., 3-necked flask equipped with stirrer and condenser. The mixture boiled vigorously and external cooling was required. When the reaction had subsided, heat was applied by a steam-bath for one hour. The reaction mixture was then cooled, diluted with 10 ml. of water and filtered. The precipitate was dissolved in aqueous base, the solution was filtered and acidified with sulfuric acid. The colorless solid was filtered and dried and melted at 182–183°. The melting point of a mixture of the compound with anisic acid showed no depression.

1,4,5,6-Tetrachloro[2.2.1]bicyclohept-4-ene-2,3-dicarboxylic Acid.—A mixture of 20.3 g. of 1,2,3,4-tetrachlorocyclopentadiene and 10 g. of maleic anhydride in 40 ml. of benzene was refluxed for 6 hours. The reaction mixture was steam distilled to remove the solvent and to hydrolyze the anhydride. Thirty grams (94%) of colorless crystals which melted at 198–200° separated from the aqueous solution. The analytical sample was crystallized twice from distilled water.

Anal. Calcd. for $C_9H_6Cl_4O_4$: Cl, 44.37; neut. equiv., 160. Found: Cl, 44.3, 44.4; neut. equiv., 162.

1,2,3,4-Tetrachloro-1,4,4a,8a-tetrahydro-1,4-methanonaphthalene-5,8-dione.—1,2,3,4-Tetrachlorocyclopentadiene (20.3 g.), *p*-benzoquinone (10.6 g.) and 40 ml. of ethylbenzene were mixed and refluxed for 13 hours at about 140°. The reaction mixture was cooled and filtered. The crude, pale yellow product (19.8 g., 60%) was recrystallized from ethyl alcohol and melted at 167–168°.

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(4) E. H. Prill, THIS JOURNAL, **69**, 62 (1947); Velsicol Corporation, British Patent 614,931 (December 30, 1948); S. H. Herzfeld, R. E. Lidov and H. Bluestone, to Velsicol Corporation, U. S. Patent 2,606,910 (August 12, 1952); E. T. McBee, H. Rakoff and R. K. Meyers, THIS JOURNAL, **77**, in press.

(5) All temperatures are uncorrected.

Anal. Calcd. for $C_{11}H_6Cl_4O_2$: Cl, 45.5. Found: Cl, 45.4, 45.7.

4,5,6,7-Tetrachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene.—A solution of 150 g. (0.75 mole) of 1,2,3,4-tetrachlorocyclopentadiene in 100 ml. of benzene was stirred and refluxed on a steam-bath and 55 g. of cyclopentadiene was added dropwise during 2 hours. An additional 15 g. of cyclopentadiene was added and the solution was refluxed for 12 hours. The benzene was removed by distillation and the residue was then distilled under reduced pressure to give 155 g. (76%) of adduct, b.p. 105–110° (2–3 mm.). Fractional distillation from a Vigreux column yielded pure liquid, b.p. 100–101° (2 mm.), $n^{20}D$ 1.5533.

Anal. Calcd. for $C_{10}H_8Cl_4$: C, 44.5; H, 2.96. Found: C, 44.5; H, 2.94.

Chlorination of 27 g. of adduct with 9 g. of chlorine in 125 ml. of carbon tetrachloride gave two products: (1) b.p. 116–118° (2 mm.) (6.5 g.), m.p. 63–64°.

Anal. Calcd. for $C_{10}H_7Cl_5$: C, 39.4; H, 2.30. Found: C, 39.0; H, 2.52.

(2) b.p. 148–151° (3 mm.) (8.0 g.).

Anal. Calcd. for $C_{10}H_7Cl_7$: Cl, 66.2. Found: Cl, 66.0.

Acknowledgment.—The authors are indebted to the Hooker Electrochemical Company for financial assistance in this investigation and to H. E. Ungnade and R. D. Crain for assistance in the preparation of the manuscript.

West Lafayette, Indiana

[Contribution from the Department of Chemistry, Purdue University]

1,2,3,4-Tetrachlorocyclopentadiene. II. The Action of Sulfuric Acid on the Diene

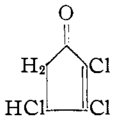
By E. T. McBee and R. K. Meyers[1]

Received July 16, 1954

Concentrated sulfuric acid reacts with 1,2,3,4-tetrachlorocyclopentadiene at room temperature to give an unsaturated ketone which is assigned the structure of 2,3,4-trichloro-2-cyclopentenone. The reactions of the ketone are discussed.

Discussion

The action of concentrated sulfuric acid on 1,2,3,4-tetrachlorocyclopentadiene[2] at room temperature gives an 80% yield of an unsaturated ketone $C_5H_3Cl_3O$ (I), m.p. 27–28°. The ultraviolet absorption spectrum shows this ketone to be conjugated. On bromination it absorbs first one mole of bromine, then more slowly a second, with elimination of hydrogen bromide. The structures of the unsaturated ketone and its bromination products are therefore assigned as



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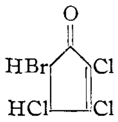

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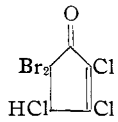
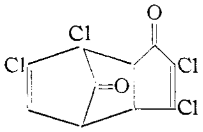


III

The ketone I is dehydrohalogenated with sodium acetate. The expected dienone is isolated as the dimer (IV or IVa).[3]



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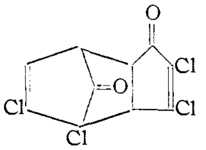
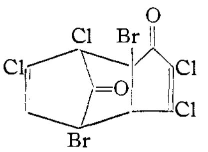
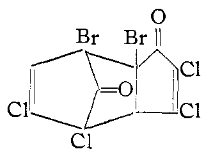


IV IVa

Thermal degradation of IV gives carbon monoxide, hydrogen chloride and $C_{18}H_7Cl_7O_2$ instead of the expected dihydroindone. It is believed that the intermediate dihydroindone is dimerized.

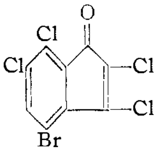


V



Va

The bromoketone II is dehydrohalogenated in the same fashion to give a diketone V (or Va), which loses carbon monoxide and hydrogen bromide on heating in xylene to give an indone C_9HBrCl_4O (VI or VIa).[4]



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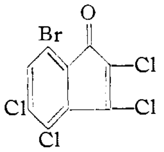

VI VIa

Experimental

2,3,4-Trichloro-2-cyclopentenone.—A mixture of 306 g. (1.5 moles) of 1,2,3,4-tetrachlorocyclopentadiene and 350 ml. of concentrated sulfuric acid was stirred at room temperature. After 5 hours the homogeneous reaction mixture was poured onto chipped ice. The organic layer was separated and the aqueous layer was extracted with 250 ml. of chloroform. The chloroform solution was added to the organic material, washed five times with 100-ml. portions of water, and dried over sodium sulfate and Drierite. The chloroform was removed by distillation and the remaining liquid was distilled under reduced pressure to give 10 g. of forerun, b.p. 82–85° (1.5 mm.), and 213 g. (81.4%) of ketone, b.p. 84–85° (1.5 mm.), $n^{20}D$ 1.5569. The distillate was crystallized from petroleum ether (b.p. 35–37°) and melted at 27–28°, $\lambda_{\max}$ 243 mμ (log ε 4.12), $\lambda_{\max_2}$ 315 mμ (log ε 1.66) (in ethanol).

Anal. Calcd. for $C_5H_3Cl_3O$: C, 32.3; H, 1.62. Found: C, 32.4; H, 1.62.

Tetrachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene-1,8-dione.—2,3,4-Trichloro-2-cyclopentenone (40 g., 0.22 mole), dissolved in 100 ml. of glacial acetic acid, was treated with 30 g. of sodium acetate with stirring. The mixture turned dark immediately upon the addition of the sodium acetate and evolved heat. After one hour, the mixture was diluted with water and filtered with suction. A small amount of oil, which separated from the filtrate, was dissolved in 25 ml. of acetic acid and treated again with 10 g. of sodium acetate. The combined products were crystallized from benzene giving 13 g. of nearly colorless solid, m.p. 180–182° dec. Two recrystallizations from benzene gave colorless crystals which

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(1) In part from the Ph.D. Thesis of R. K. Meyers, Purdue University, February, 1950.

(2) E. T. McBee, R. K. Meyers and C. F. Baranauckas, This Journal, **76**, 86 (1954).

(3) *Cf.* C. F. H. Allen, *Chem. Revs.*, **37**, 209 (1954).

(4) It is assumed in the dimerizations that the unsubstituted or mono-substituted double bond will be a better dienophile than the di-substituted double bond. Perchlorocyclopentadiene reacts with cyclopentadiene as the diene, the latter as dienophile [H. Holst and V. Stolp, *Z. Naturforsch*, **7b**, 635 (1952); *cf.*, R. Riemschneider, *ibid.*, **6B**, 396 (1951)].