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

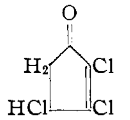
By E. T. McBee and R. K. Meyers[1]

Received July 16, 1954

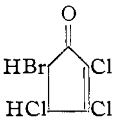
Concentrated sulfuric acid reacts with 1,2,3,4-tetrachlorocyclopentadiene at room temperature to give an unsaturated ketone which is assigned the structure of 2,3,4-trichloro-2-cyclopentenone. The reactions of the ketone are discussed.

Discussion

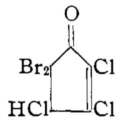
The action of concentrated sulfuric acid on 1,2,3,4-tetrachlorocyclopentadiene[2] at room temperature gives an 80% yield of an unsaturated ketone $C_5H_3Cl_3O$ (I), m.p. 27–28°. The ultraviolet absorption spectrum shows this ketone to be conjugated. On bromination it absorbs first one mole of bromine,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



I

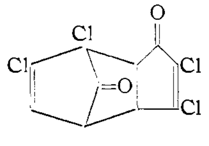


II



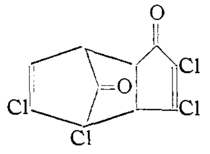
III

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



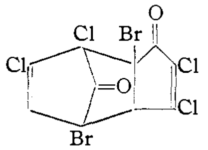
IV

or

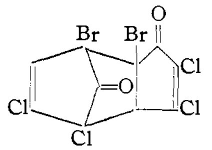


IVa

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.

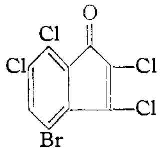


V



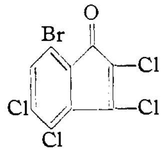
Va

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]



VI

or



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°, λ_{max} 243 mμ (log ϵ 4.12), λ_{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 disubstituted 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)].

melted at 184–185° with the evolution of gas and the formation of a yellow liquid.

Anal. Calcd. for $C_{10}H_4Cl_4O_2$: C, 40.2; H, 1.34. Found: C, 40.0; H, 1.34.

On refluxing in xylene, the dione decomposed with the evolution of hydrogen chloride. The xylene was removed by distillation and the residual tan solid was crystallized from ligroin (b.p. 90–100°) to give a colorless micro-crystalline compound, m.p. 262–264°.

The same compound was obtained by heating the dione at its melting point until the evolution of gas ceased.

Anal. Calcd. for $C_{18}H_7Cl_7O_2$: C, 42.9; H, 1.38; mol. wt., 503. Found: C, 43.0, 43.3; H, 1.30, 1.25; mol. wt. (Rast), 520.

5-Bromo-2,3,4-trichloro-2-cyclopentenone.—A solution of 30 g. (0.19 mole) of bromine in 50 ml. of carbon tetrachloride was added dropwise to a refluxing solution of 35 g. (0.19 mole) of 2,3,4-trichloro-2-cyclopentenone in 50 ml. of carbon tetrachloride. Hydrogen bromide was evolved during the addition which required 2.5 hours. The reaction mixture was dried over Drierite and distilled to remove the solvent. Vacuum distillation of the residue yielded 42 g. (91%) of bromoketone boiling at 93–100° (3 mm.). On redistillation of the product from a Vigreux column, almost the entire amount distilled at 89–91° (2 mm.), $n^{20}D$ 1.5848.

Anal. Calcd. for $C_5H_2BrCl_3O$: C, 22.7; H, 0.75. Found: C, 22.8; H, 0.76.

Dehydrochlorination of 5-Bromo-2,3,4-trichloro-2-cyclopentenone.—A mixture of 10 g. (0.041 mole) of 5-bromo-2,3,4-trichloro-7-cyclopentenone, 7.5 g. of sodium acetate and 10 ml. of glacial acetic acid was shaken at room temperature. Heat was evolved and the mixture turned green. After one hour, the mixture was diluted with an equal volume of water and filtered with suction. The colorless solid was crystallized from petroleum ether (b.p. 90–100°) giving 2.1 g. (21%) of diketone, m.p. 170–171° dec.

Anal. Calcd. for $C_{10}H_2Br_2Cl_4O_2$: C, 26.3; H, 0.44. Found: C, 25.8, 26.0; H, 0.54, 0.59.

Bromotetrachloro-1-indone.—A mixture of 1.2 g. of the preceding compound (m.p. 170–171°) and 5 ml. of xylene was refluxed for 2 hours. Hydrogen bromide was evolved, first rapidly, then more slowly until the reaction was complete. The xylene was removed and the residue was crystallized three times from petroleum ether–benzene to give 0.3 g. of yellow needles, m.p. 156–157°.

Anal. Calcd. for C_9HBrCl_4O: C, 31.2; H, 0.29; mol. wt., 347. Found: C, 31.0, 31.1; H, 0.29, 0.32; mol. wt., 356.

Dibromo-2,3,4-trichloro-2-cyclopentenone.—A solution of 50 g. (0.31 mole) of bromine in 50 ml. of carbon tetrachloride was added dropwise to a refluxing solution of 25 g. (0.13 mole) of 2,3,4-trichloro-2-cyclopentenone in 50 ml. of carbon tetrachloride. The reaction proceeded first rapidly with evolution of hydrogen bromide, then more slowly. Part of the carbon tetrachloride was therefore removed by distillation and replaced with 50 ml. of glacial acetic acid. The remainder of the bromine solution was added and the mixture was heated on a steam-bath overnight. Unreacted bromine and carbon tetrachloride were removed and the remaining acetic acid solution was diluted with water. The mixture was extracted with chloroform and the chloroform solution was dried over sodium sulfate. The solvent was removed and the residue was distilled under reduced pressure to give 32 g. (70%) of dibromoketone boiling at 109–113° (2 mm.). Redistillation from a Vigreux column gave an analytical sample, b.p. 112–113° (2 mm.), $n^{20}D$ 1.6227.

Anal. Calcd. for $C_5HBr_2Cl_3O$: C, 17.5; H, 0,29. Found: C, 17.3; H, 0.28.

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

W. LAFAYETTE, INDIANA

[CONTRIBUTION FROM THE ROHM AND HAAS COMPANY, REDSTONE ARSENAL RESEARCH DIVISION]

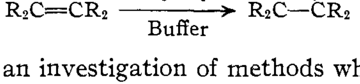
Peroxytrifluoroacetic Acid. IV. The Epoxidation of Olefins[1]

BY WILLIAM D. EMMONS AND ANGELO S. PAGANO

RECEIVED JULY 21, 1954

Satisfactory procedures have been developed for the epoxidation of olefins and negatively substituted olefins with peroxytrifluoroacetic acid. These procedures are dependent on the presence of a buffer such as dibasic sodium phosphate, sodium carbonate, or sodium bicarbonate in the reaction medium. The epoxidation of olefins with peroxytrifluoroacetic acid has substantial advantages over previously described methods of epoxidation.

Peroxytrifluoroacetic acid has been found to be a remarkably efficient reagent for olefin epoxidation and indeed offers a number of advantages over previously known methods. The effectiveness of peroxytrifluoroacetic acid as a hydroxylation reagent for the preparation of α-glycols from olefins[2]



$$R_2C{=}CR_2 \xrightarrow[\text{Buffer}]{CF_3CO_3H} R_2C\overset{O}{—}CR_2$$

prompted an investigation of methods which could be employed for isolation of the epoxide intermediates. Peracetic and particularly perbenzoic acid have been widely used for expoxidation of olefins[3]; however, both of these reagents have inherent limitations to their use which peroxytrifluoroacetic acid does not have.

The utilization of peroxytrifluoroacetic acid as an olefin epoxidation reagent is dependent on the fact that the peracid is apparently a much weaker acid than trifluoroacetic acid itself. Efforts to obtain quantitative information regarding this point have been unsuccessful since peroxytrifluoroacetic acid reacts very rapidly with water to form hydrogen peroxide. While this reaction is reversible, qualitative evidence indicates that the equilibrium lies well to the right. However, the dissociation con-

$$CF_3CO_3H + H_2O \rightleftarrows CF_3CO_2H + H_2O_2$$

stants of both performic and peracetic acids have been measured, and the *pK* values are 7.1 and 8.2, respectively.[4] The values for formic and acetic acids are 3.7 and 4.8 so in each case there is a difference of 3.4 in the *pK* values for the acid and the corresponding peracid. On this basis then it is reasonable to assume that peroxytrifluoroacetic acid is a much weaker acid than trifluoroacetic acid

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[1] This research was carried out under Army Ordnance Contract W-01-021-ORD-334.

[2] W. D. Emmons, A. S. Pagano and J. P. Freeman, THIS JOURNAL, **76**, 3472 (1954).

[3] D. Swern, "Organic Reactions," Vol. VII, John Wiley and Sons, Inc., New York, N. Y., 1953, p. 378.

[4] A. J. Everett and G. S. Minkoff, *Trans. Faraday Soc.*, **49**, 410 (1953).