A total of 10 g. (14%) of 1,1,8,8-tetrafluoroöctachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene (III) was recovered from the pot residue by crystallizing from acetone and melted at 280–281°.

Anal. Calcd. for $C_{10}Cl_8F_4$: C, 25.05; H, 0.0; mol. wt., 480. Found: C, 24.98; H, 0.08; mol. wt. (vapor pressure lowering in tetrahydrofuran) 488, 493.

Diels–Alder Adducts of 5,5-Difluorotetrachlorocyclopentadiene (II).—The adducts of II with styrene and *p*-chlorostyrene were prepared by mixing equivalent amounts of the diene and dienophile. An exothermic reaction occurred within two minutes. The *p*-chlorostyrene adduct was crystallized from petroleum ether (b.p. 30–60°). The styrene adduct was distilled, b.p. 149° (15 mm.) and the distillate crystallized after standing for two days. Colorless prisms were obtained from petroleum ether (b.p. 60–70°). The acrylic acid adduct of II was prepared by heating equivalent amounts of the diene and dienophile for 90 minutes. The product was crystallized from hot water. The maleic anhydride adduct of II was prepared by slowly adding II to slightly more than one equivalent of maleic anhydride heated to 90°. The product crystallized as needles from hot water. The adducts of II with *p*-benzoquinone and cyclopentadiene were prepared by refluxing equivalent amounts of diene and dienophile in petroleum ether. The *p*-benzoquinone adduct was crystallized from methanol. The cyclopentadiene adduct was distilled, b.p. 110–115° (4 mm.), and the product solidified on cooling.

Dimethyl 7,7-Difluoro-1,4,5,6-tetrachlorobicyclo[2.2.1]-2,5-heptadiene-2,3-dicarboxylate (IV).—Dimethyl acetylenedicarboxylate[18] (10.6 g., 0.075 mole) and 5,5-difluorotetrachlorocyclopentadiene (II) (18.0 g., 0.075 mole) were heated together to 120° when a vigorous reaction occurred and the temperature of the mixture rose rapidly to 175°. The mixture was cooled and crystallized from petroleum ether (b.p. 30–60°) to give 13.0 g. (46%) of colorless needles, m.p. 71–72°.

Anal. Calcd. for $C_{11}H_6Cl_4F_2O_4$: C, 34.59; H, 1.58. Found: C, 34.55; H, 1.49.

Some of the dimer III of 5,5-difluorotetrachlorocyclopentadiene (5 g.) was recovered from the mother liquor.

Pyrolysis of Dimethyl 7,7-Difluoro-1,4,5,6-tetrachlorobicyclo[2.2.1]-2,5-heptadiene-2,3-dicarboxylate (IV).—The finely powdered adduct from dimethyl acetylenedicarboxylate (IV) (7.08 g.) was pyrolyzed in an atmosphere of purified nitrogen in small portions in a 1 × 12-inch Pyrex tube heated at 480°. The product, 5.4 g. (83%) of gray solid, was collected in a Dry Ice trap. Several crystallizations from petroleum ether (b.p. 30–60°) and methanol gave colorless needles, m.p. and mixed m.p. with authentic dimethyl tetrachlorophthalate,[19] 92.0–92.6°.

Anal. Calcd. for $C_{10}H_6Cl_4O_4$: C, 36.18; H, 1.82. Found: C, 35.94; H, 2.08.

5,5-Difluoro-2-methoxy-1,3,4-trichlorocyclopentadiene (V).—A solution of II (18.0 g., 0.075 mole) in 200 ml. of methanol was slowly treated with a solution of potassium hydroxide (8.41 g., 0.150 mole) in 250 ml. of methanol at room temperature. Filtration gave 4.95 g. (92%) of potassium chloride, which was free from fluoride. The filtrate was added to 500 ml. of water and extracted with petroleum ether (b.p. 30–60°). The solvent was removed from the dried extract under reduced pressure and the residue was distilled to give 13.7 g. (77%) of liquid, b.p. 59–62° (1.5 mm.), $n^{20}D$ 1.4755, $\lambda_{max.}$ 268 mμ, log ϵ 3.36. To a solution of 2.35 g. (0.01 mole) of this product in 50 ml. of petroleum ether (b.p. 90–100°) was added 1.00 g. (0.01 mole) of maleic anhydride and the mixture was refluxed for 18 hours. On cooling, 2.7 g. (81%) of crystalline solid separated. Recrystallization from the same solvent gave colorless prisms, m.p. 133–134.5°.

Anal. Calcd. for $C_{10}H_5Cl_3F_2O_4$: C, 36.01; H, 1.51; neut. equiv., 166.8. Found: C, 36.10; H, 1.52; neut. equiv., 165.7.

4,4-Difluoro-2,3,5-trichloro-2-cyclopentenone (VI).—5,5-Difluorotetrachlorocyclopentadiene (24.0 g., 0.10 mole) was added slowly with stirring to 148.4 g. (1.48 moles) of fluorosulfonic acid at 115–120°. The product was poured onto 500 g. of crushed ice and extracted with petroleum ether (b.p. 30–60°). The extract was washed with water, dried and distilled. A total of 9.8 g. (45%) of colorless liquid was collected, b.p. 64–66° (4 mm.), $\lambda_{max.}$ 241 mμ (log ϵ 4.13); $\lambda_{max.}$ 324 mμ (log ϵ 1.42); $\lambda_{max.}$ 5.80 μ (C=O) and $\lambda_{max.}$ 6.40 μ (C=C).

Anal. Calcd. for $C_5HCl_3F_2O$: C, 27.13; H, 0.46. Found: C, 26.97; H, 0.32.

This ketone also was obtained by treating 14.7 g. of 5,5-difluoro-2-methoxy-1,3,4-trichlorocyclopentadiene with 40 g. of 75% sulfuric acid at 0°. The organic phase was decanted and distilled, b.p. 64–68° (4 mm.). The ketones had identical infrared and ultraviolet spectra.

Acknowledgments.—The authors wish to thank the Hooker Electrochemical Company for financial assistance in this work.

LAFAYETTE, INDIANA

---

(18) E. H. Huntress, T. E. Lesslie and J. Bornstein, *Org. Syntheses*, **32**, 55 (1952).

(19) C. Graebe, *Ann.*, **340**, 245 (1905).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

The Reduction of Hexachlorocyclopentadiene. 1,2,3,4,5-Pentachlorocyclopentadiene[1]

BY E. T. MCBEE AND D. K. SMITH

RECEIVED AUGUST 2, 1954

The catalytic hydrogenation of hexachlorocyclopentadiene (I) proceeds stepwise to give 1,2,3,4,5-pentachlorocyclopentadiene (II) and 1,2,3,4-tetrachlorocyclopentadiene (III). The reduction of hexachlorocyclopentadiene with lithium aluminum hydride at −40° gives II, which is not reduced further by this reagent. The pentachloro compound II is also obtained from I by reduction with stannous chloride in acetone. Diels–Alder adducts have been prepared from II and suitable dienophiles.

Introduction

It has been shown previously that hexachlorocyclopentadiene (I) can be reduced to 1,2,3,4-tetrachlorocyclopentadiene (III) with zinc and hydrochloric acid.[2] The diene III has been studied[3] extensively and its structure is well established.

A pentachlorocyclopentadiene has been obtained in small yield as a by-product in the chlorination of cyclopentadiene with sodium hypochlorite,[4,5] and in the reduction of hexachlorocyclopentadiene (I) with zinc and hydrochloric acid.[4] The structures of these compounds are uncertain and a definite identification is not possible until additional experimental data are available.

---

(1) Abstracted from a portion of a thesis submitted by Delmont K. Smith to the Graduate School of Purdue University in partial fulfillment of the requirements for the Ph.D. degree.

(2) E. T. McBee, R. K. Meyers and C. F. Baranauckas, THIS JOURNAL, **77**, 86 (1955).

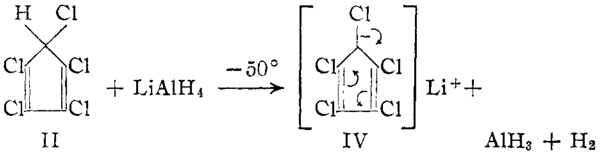
(3) R. K. Meyers, Ph.D. Thesis, Purdue University, 1950.

(4) R. Riemschneider, *Z. Naturforsch.*, **6B**, 463 (1951).

(5) F. L. Straus, L. Kolleck and W. Heyn, *Ber.*, **63**, 1868 (1930).

1,2,3,4,5-Pentachlorocyclopentadiene (II) is obtained by catalytic hydrogenation of hexachlorocyclopentadiene with platinum oxide in ethanol. The hydrogenation proceeds stepwise to give II and 1,2,3,4-tetrachlorocyclopentadiene (III) after absorption of one and two equivalents of hydrogen, respectively. Further hydrogenation of III gives cyclopentane. For preparative purposes, 1,2,3,4,5-pentachlorocyclopentadiene (II) is best obtained by reduction of I with stannous chloride in acetone.

Although I is decomposed by basic reagents, it is smoothly reduced to II by an ether solution of lithium aluminum hydride at −50°. Treatment of II with lithium aluminum hydride at −50° gives one equivalent of hydrogen gas and II is recovered on hydrolysis of the reaction mixture. This reaction is interpreted as the formation of a pentachlorocyclopentadienyl carbanion (IV), which would be stabilized by resonance in a manner similar to the cyclopentadienyl carbanion.[6] The ion IV is apparently unstable at 0° or above, since the reduction of I with lithium aluminum hydride at these temperatures gives only decomposition products. The formation of IV would explain the failure to obtain 1,2,3,4-tetrachlorocyclopentadiene by reduction with lithium aluminum hydride, since the AlH_4^- ion could not attack the carbanion IV.

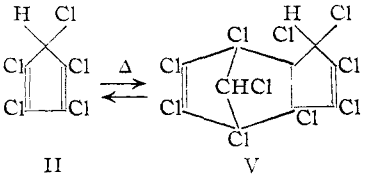


II IV

1,2,3,4,5-Pentachlorocyclopentadiene is obtained also by reduction of octachlorocyclopentene with lithium aluminum hydride or by catalytic hydrogenation. The latter reaction proceeds *via* I and can also give III on continued hydrogenation.

The structure of the diene II is established by its conversion to 1,2,3,4-tetrachlorocyclopentadiene. It is further confirmed by the ultraviolet absorption spectra of II (λ_{max} 307 mμ, log ϵ 3.28) compared with those of I (λ_{max} 323 mμ, log ϵ 3.17) and III (λ_{max} 274 mμ, log ϵ 3.69)[7] and the methods of preparation.

The diene II is identified easily by its crystalline dimer V which forms slowly at room temperature. The dimer V is depolymerized in excellent yield by heating at 340°. This process provides a good method for preparing pure II. In view of its facile and reversible formation, V is regarded as a Diels–Alder type of adduct analogous to dicyclopentadiene,[8] with the structure of 1,2,3,3a,4,5,6,7,7a,8-decachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene (V). The diene II forms Diels–Alder adducts also with maleic anhydride and cyclopentadiene. Chlorination of the latter adduct in the presence of anhydrous aluminum chloride gives an octachloromethanoindene, analogous to the component Nonachlor, of Chlordan insecticide.[9] Methanolic sodium hydroxide causes extensive decomposition of II. With concentrated sulfuric acid at 120°, II gives only the dimer V.



II V

Experimental[10]

1,2,3,4,5-Pentachlorocyclopentadiene (II). Catalytic Hydrogenation of Hexachlorocyclopentadiene (I).—A mixture of 27.3 g. (0.1 mole) of hexachlorocyclopentadiene (I), 35 ml. of absolute ethanol and 0.081 g. of platinum dioxide was shaken with hydrogen at 55.2 p.s.i. A total of 0.113 mole (8.5 p.s.i.) of hydrogen was absorbed within 15 minutes. Distillation of the product gave a yellow liquid, b.p. 68–78° (1.5 mm.), which yielded 10.0 g. of 1,2,3,3a,4,5,6,7,7a,8-decachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene (V) on standing for two weeks. An additional 7.0 g. of V was obtained from the distillation residue. The dimer was crystallized from petroleum ether (b.p. 30–60°) to give large, colorless prisms, m.p. 217–218°, total yield 71%.

Anal. Calcd. for $C_{10}H_2Cl_8$: C, 25.15; H, 0.42; mol. wt., 477. Found: C, 25.24; H, 0.78; mol wt., 488 (vapor pressure lowering in tetrahydrofuran).

Finely powdered V (23.8 g.) was pyrolyzed in an atmosphere of purified nitrogen in small portions in a 1 × 12-inch Pyrex tube heated at 340–350°. The product (22.9 g.) was collected in a Dry Ice trap. Distillation gave 21.1 g. (89%) of 1,2,3,4,5-pentachlorocyclopentadiene, b.p. 84–87° (4 mm.), and 1.3 g. of the dimer was recovered from the distillation residue.

Lithium Aluminum Hydride Reduction of Hexachlorocyclopentadiene.—A solution of lithium aluminum hydride (0.276 mole) in anhydrous ether was added slowly to a solution of 54.6 g. (0.2 mole) of hexachlorocyclopentadiene (I) in 300 ml. of anhydrous ether at −50°. After completion of the addition, the clear reaction mixture was poured immediately onto a mixture of crushed ice and concentrated hydrochloric acid. The organic product was extracted with ether and the dried extract was distilled to give 31.7 g. (66.7%) of yellow diene II, b.p. 84–86° (4 mm.), n^{20}_D 1.5610, λ_{max} 307 mμ, log ϵ 3.28.

Anal. Calcd. for C_5HCl_5: C, 25.15; H, 0.42. Found: C, 24.86; H, 0.54.

An additional 10.3 g. of the product was isolated as the dimer V from the distillation residue to give a total yield of 88.3%.

Lithium Aluminum Hydride Reduction of Octachlorocyclopentene.—A lithium aluminum hydride solution (0.28 mole) in anhydrous ether was added slowly to a solution of 34.4 g. (0.1 mole) of octachlorocyclopentene in 1000 ml. of ether at −50°. The resulting solution was poured immediately onto a mixture of crushed ice and concentrated hydrochloric acid. The organic material was extracted with ether and dried. This solution was distilled to give 5.3 g. of 1,2,3,4,5-pentachlorocyclopentadiene (II), b.p. 110–115° (6 mm.) and 12.3 g. of the dimer V from the distillation residue (total yield 74%).

Reduction of Hexachlorocyclopentadiene with Stannous Chloride.—A solution of 225.7 g. (1.0 mole) of stannous chloride dihydrate in 350 ml. of acetone was added slowly to a solution of 273 g. (1.0 mole) of hexachlorocyclopentadiene in 100 ml. of acetone. After completion of the exothermic reaction, the mixture was poured into 1000 ml. of water. The organic material was extracted with ether and the dried extract distilled to give 121.0 g. of distillate, which gave 98.2 g. of dimer V on standing for a few days. An additional 68.0 g. of the dimer V was recovered from the distillation residue (total yield 70%).

1,2,3,4-Tetrachlorocyclopentadiene (III). Catalytic Hydrogenation of Hexachlorocyclopentadiene.—The absorp-

---

[6] G. W. Wheland, "The Theory of Resonance," John Wiley and Sons, Inc., New York, N. Y., 1944, p. 173.

[7] E. T. McBee, C. W. Roberts and J. D. Idol, Jr., in press.

[8] P. J. Wilson, Jr., and J. H. Wells, *Chem. Revs.*, **34**, 1 (1944).

[9] S. J. Cristol, *Advances in Chem. Ser.*, **1**, 183 (1950).

[10] The analyses were determined by Mrs. P. T. Yeh of Purdue University. All temperatures are uncorrected.

tion of 2.73 molar equivalents of hydrogen by a mixture of 27.3 g. (0.1 mole) of hexachlorocyclopentadiene (I), 30 ml. of absolute ethanol and 0.100 g. of platinum dioxide was completed in 80 minutes. The reaction mixture was filtered and cooled with Dry Ice and the crystallized product was removed by filtration. Two crystallizations from petroleum ether (b.p. 35–37°) gave 10.0 g. (49%) of 1,2,3,4-tetrachlorocyclopentadiene (III), m.p. and mixed m.p. 60–62°.[2]

Catalytic Hydrogenation of 1,2,3,4,5-Pentachlorocyclopentadiene.—A mixture of 18.8 g. (0.079 mole) of 1,2,3,4,5-pentachlorocyclopentadiene, 35 ml. of absolute ethanol and 0.15 g. of platinum dioxide was hydrogenated until 0.086 mole of hydrogen was absorbed. The mixture was filtered and cooled with Dry Ice to yield 6.0 g. (38%) of 1,2,3,4-tetrachlorocyclopentadiene, m.p. and mixed m.p. 60–62.5°.

Catalytic Hydrogenation of Octachlorocyclopentene.—The hydrogenation of a mixture of 34.4 g. (0.1 mole) of octachlorocyclopentene, 100 ml. of absolute ethanol and 0.100 g. of platinum dioxide was stopped after one hundred minutes and absorption of 3.8 molar equivalents of hydrogen. The reaction mixture was filtered and cooled with Dry Ice to give 7.9 g. of 1,2,3,4-tetrachlorocyclopentadiene, m.p. and mixed m.p. 60–62°. An additional 2.0 g. of this product was obtained by distillation of the filtrate. The total yield was 49%.

Catalytic Hydrogenation of 1,2,3,4-Tetrachlorocyclopentadiene.—A mixture of 10.2 g. (0.05 mole) of 1,2,3,4-tetrachlorocyclopentadiene, 50 ml. of absolute ethanol and 0.161 g. of platinum dioxide was hydrogenated until 5.0 molar equivalents of hydrogen was absorbed. The resulting mixture was filtered and distilled to give 2.4 g. (69%) of liquid, b.p. 45–50°, n^{20}D 1.4045. This material was washed with water, dried and distilled. The distillate gave an infrared spectrum identical with that of cyclopentane.[11]

Attempted Reduction of 1,2,3,4,5-Pentachlorocyclopentadiene with Lithium Aluminum Hydride.—1,2,3,4,5-Pentachlorocyclopentadiene (16.5 g., 0.0694 mole) in 100 ml. of anhydrous ether was treated with an ether solution of lithium aluminum hydride (0.165 mole) at −50°. A total of 1.789 liters (0.0718 mole) of gas was liberated. The reaction mixture was hydrolyzed by pouring it onto a mixture of crushed ice and concentrated hydrochloric acid. The organic product was extracted with ether and dried. The extract was distilled to give 12.5 g. of liquid distillate which completely dimerized to V, m.p. and mixed m.p. 215–218°. An additional 2.5 g. of V was recovered from the distillation residue (total recovery 94%).

1,4,5,6,7-Pentachlorobicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic Acid.—Maleic anhydride (3.44 g., 0.35 mole) and 6.5 g. (0.0262 mole) of 1,2,3,4,5-pentachlorocyclopentadiene were heated to 120° when a vigorous reaction occurred and the temperature of the mixture rose rapidly to 200°. The mixture was cooled and recrystallized from water to give 6.8 g. (69%) of colorless needles, m.p. 183–184.5°.

Anal. Calcd. for $C_9H_5Cl_5O_4$: C, 30.50; H, 1.42; neut. equiv., 177.2. Found: C, 30.19; H, 1.70; neut. equiv., 179.2

4,5,6,7,8-Pentachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene.—Cyclopentadiene (9.9 g., 0.15 mole) was added slowly to a refluxing solution of 35.7 g. (0.15 mole) of 1,2,3,-4,5-pentachlorocyclopentadiene (II) in 200 ml. of petroleum ether (b.p. 60–70°). The solvent was removed under reduced pressure and the residue was crystallized on cooling. This material (26.2 g., 57.5%) was crystallized twice from petroleum ether (b.p. 30–60°) to give colorless plates, m.p. 100–101°.

Anal. Calcd. for $C_{10}H_7Cl_5$: C, 39.45; H, 2.32. Found: C, 39.69; H, 2.37.

Chlorine gas was passed through a mixture of 7.76 g. (0.0207 mole) of 4,5,6,7,8-pentachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene, 35 ml. of carbon tetrachloride and 0.2 g. of anhydrous aluminum chloride at room temperature for 160 minutes. After filtering the mixture, the solvent was removed and the residue was crystallized from petroleum ether (b.p. 30–60°) to give colorless plates, m.p. 150–151°.

Anal. Calcd. for $C_{10}H_6Cl_8$: C, 29.36; H, 1.46. Found: C, 29.50; H, 1.95.

Acknowledgments.—The authors wish to thank the Hooker Electrochemical Company for financial support of this work and to acknowledge the assistance of Dr. H. E. Ungnade.

LAFAYETTE, INDIANA

---

[11] Catalog of Infrared Spectral Data, American Petroleum Institute Research Project 44, serial number 254.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF EMORY UNIVERSITY]

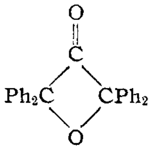
sym-Tetraphenylacetone. III. The Preparation of 2,2,4,4-Tetraphenyloxetanone

BY G. BROOKE HOEY,[1a,b] DOUGLAS O. DEAN[1a,c] AND CHAS. T. LESTER[2]

RECEIVED JULY 21, 1954

The autoöxidation of tetraphenylacetone under a variety of conditions, the presence of strong base excepted, produces a heterocyclic ketone, 2,2,4,4-tetraphenyloxetanone. The structure of the ketone has been established by its chemical reactions, its degradation products and the infrared spectrograms of the ketone and three alcohols produced from it.

In a previous publication[3] we reported that *sym*-tetraphenylacetone (I) was cleaved by oxygen in the presence of base to give an essentially quantitative yield of diphenylacetic acid and benzophenone. We wish now to report that the autoxidation of I in acetic acid gives a lesser amount of cleavage products and a substantial yield of a dioxo compound to which we have assigned the structure, 2,2,4,4-tetraphenyloxetanone (II).


II

This compound has appeared frequently in this Laboratory as a product of the prolonged treatment of I and its derivatives under a variety of reaction conditions.[4] Some examples of its synthesis are recorded in Table I.

II was described some years ago by Vorlander[5] as the product of the oxidation of tetraphenylallene. On the basis of its analysis and

---

[1] (a) Taken in part from the Ph.D. Dissertations of G. B. Hoey, Emory University, 1954, and D. O. Dean, Emory University, 1950; (b) Tennessee Eastman Fellow, 1952–1953; (c) supported in part by a contract with the Office of Naval Research.

[2] Responsible co-author.

[3] D. O. Dean, W. B. Dickinson, G. B. Hoey and C. T. Lester, THIS JOURNAL, 76, 4988 (1954).

[4] II was first isolated in very small yield from a 0.001 *M* solution of α-bromo-*sym*-tetraphenylacetone in pyridine which had been heated for several weeks; W. B. Dickinson, M.S. thesis, Emory University, 1947.

[5] D. Vorlander and P. Winstein, *Ber.*, 56, 1122 (1923).