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]2-heptene-7-ol which did not depress the melting point of an authentic sample.

5-Bromomethyl-1,2,3,4-tetrachlorobicyclo[2.2.1]2-heptene-7-one.—The cleavage of 5-bromomethyl-7,7-dimethoxy-1,2,3,4-tetrachlorobicyclo[2.2.1]2-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 $C_8H_5BrCl_4O$: C, 28.32; H, 1.49. Found: C, 28.32; H, 1.48.

7,7-Dimethoxy-1,4,5,6-Tetrachlorobicyclo[2.2.1]5-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]5-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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W. LAFAYETTE, INDIANA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

The Synthesis and Reactions of 5,5-Difluorotetrachlorocyclopentadiene[1]

BY E. T. MCBEE, D. K. SMITH AND H. E. UNGNADE

RECEIVED AUGUST 2, 1954

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 Zimmerschied[5] 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 Latif[6] 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 cyclic[7] 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

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[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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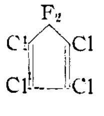
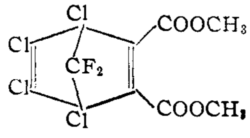
120°. On heating to 480° this compound IV gives an 83% yield of dimethyl tetrachlorophthalate. The loss of CF_2 by pyrolysis is regarded as evidence that the CF_2 group occurs in the adduct as a bridge and hence that the compounds have the structures



II



IV

Diels–Alder adducts of cyclopentadienes normally dissociate to diene and dienophile at elevated temperatures.[12] The failure of the adduct IV to dissociate in this fashion is possibly due to its high heat of formation.

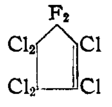
Table I

Diels–Alder Adducts of 5,5-Difluorotetrachlorocyclopentadiene

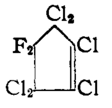
Dienophile	M.p., °C.	Yield, %	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
Maleic acid	179–180	88	30.36[a]	30.46	1.13	1.35
Acrylic acid	116–116.5	72	30.80[b]	31.08	1.29	1.50
Styrene	45–46	95	45.42	45.39	2.34	2.30
p-Chlorostyrene	90–91	75	41.24	41.29	1.87	2.01
p-Benzoquinone	125–126	56	37.97	37.86	1.16	1.34
Cyclopentadiene	39–40	74	39.25	39.20	1.98	2.29

[a] Calcd. for $C_9H_4Cl_4F_2O_4$: neut. equiv., 178.0. Found: neut. equiv., 179.4. [b] Calcd. for $C_8H_9Cl_4F_2O_2$: neut. equiv., 311.9. Found: neut. equiv., 314.7.

Since the diene II contains a CF_2 group, the difluorohexachlorocyclopentene (I) also contains such a group and has therefore structure Ia or Ib.



Ia

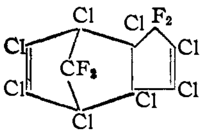


Ib

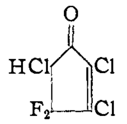
The adduct of II with cyclopentadiene adds one mole of chlorine in the presence of anhydrous aluminum chloride in carbon tetrachloride. The dimerization of the 5,5-difluorotetrachlorocyclopentadiene is regarded as a Diels–Alder reaction in view of the ease with which it occurs. The reversibility of this dimerization is comparable to the cyclopentadiene–dicyclopentadiene conversion.[13]

While the catalytic hydrogenation of hexachlorocyclopentadiene occurs rapidly and results in the stepwise replacement of the allylic chlorine atoms by hydrogen, giving successively 1,2,3,4,5-pentachlorocyclopentadiene and 1,2,3,4-tetrachlorocyclopentadiene,[10] the corresponding hydrogenation of 5,5-difluorotetrachlorocyclopentadiene (II) takes place only slowly. It stops after absorption of approximately 0.4 molar equivalent of hydrogen and the reaction mixture contains both hydrogen chloride and hydrogen fluoride. The difference in behavior of II and hexachlorocyclopentadiene is ascribed to the greater stability of the C–F linkage in II.[14a,15]

A similar difference is found in the reactivity of the dienes toward methanolic potassium hydroxide. The allylic chlorine atoms of hexachlorocyclopentadiene are displaced to give 5,5-dimethoxytetrachlorocyclopentadiene,[16] whereas II is converted to 5,5-difluoro-2-methoxy-1,3,4-trichlorocyclopentadiene (V). The presence of a conjugated system in V is established by formation of a maleic anhydride adduct. Hydrolysis of V with sulfuric acid gives a conjugated cyclopentenone as evidenced by the ultraviolet absorption spectrum. The infrared absorption spectrum (C=O frequency) is compatible only with structure VI. The methoxy group in V is therefore in the 2-position. The same ketone VI



III



VI

is formed from the reaction of the diene II with fluorosulfonic acid at 115°. It cannot be dehydrohalogenated by refluxing with sodium acetate in acetic acid and is decomposed by methanolic potassium hydroxide.

The formation of the methoxydiene V is analogous to the preparation of 2-chlorohexafluoro-1-methoxycyclopentene from 1,2-dichlorohexafluorocyclopentene.[14b] The attack of the reagent in this case and in the reaction with fluorosulfonic acid on the carbon beta to the CF_2 group is the result of the polarization of the double bond by the electronegative CF_2 group, as is the case with 1,1,1-trifluoropropene.[14a]

Experimental[17]

Difluorohexachlorocyclopentene (I).—A mixture of octachlorocyclopentene (344 g., 1.0 mole), antimony trifluoride (119 g., 0.667 mole) and antimony pentachloride (15 g., 0.05 mole) was heated for two hours at 160–170° and the resulting mixture was extracted with hydrochloric acid and water and then dried over anhydrous calcium chloride. Rectification gave 173.0 g. (58%) of difluorohexachlorocyclopentene, b.p. 93° (10 mm.), $n^{20}D$ 1.5161.

Five other polychlorocyclopentenes containing one, three, four, five and six fluorine atoms also were obtained from this reaction.

Anal. Calcd. for $C_5Cl_6F_2$: C, 19.32; H, 0.0. Found: C, 19.55; H, 0.13.

5,5-Difluorotetrachlorocyclopentadiene (II).—Difluorohexachlorocyclopentene (93.2 g., 0.3 mole) and 30 ml. of dilute (1:1) hydrochloric acid were added simultaneously to a slurry of 39.2 g. (0.6 g. atom) of zinc dust, 0.5 g. of copper sulfate and 15 ml. of water at such a rate that a reaction temperature of about 80° was maintained. The reaction mixture was filtered and the organic phase separated, washed with water and dried. Distillation gave 45 g. (63%) of 5,5-difluorotetrachlorocyclopentadiene, b.p. 45° (4 mm.), $n^{20}D$ 1.5008.

Anal. Calcd. for $C_5Cl_4F_2$: C, 25.05. Found: C, 25.20.

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(17) The melting points are uncorrected. The analyses were determined by Galbraith Microanalytical Laboratories, Knoxville, Tenn., and Mrs. P. T. Yeh, Purdue University.

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.), $n^{20}\text{D}$ 1.4755, $\lambda_{\text{max.}}$ 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.), $\lambda_{\text{max.}}$ 241 mμ (log ϵ 4.13); $\lambda_{\text{max.}}$ 324 mμ (log ϵ 1.42); $\lambda_{\text{max.}}$ 5.80 μ (C=O) and $\lambda_{\text{max.}}$ 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.

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Lafayette, Indiana

[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.

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[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.

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