1068. *Polyfluorocyclopentadienes. Part I. Synthesis of Perfluorocyclopentadiene.*

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Perfluorocyclopentadiene has been prepared by dechlorination of tetrachlorohexafluorocyclopentane, in turn prepared from perchlorocyclopentadiene.

Perfluorocyclopentadiene, prepared in 44% yield by dechlorination of 1,2,3,4-tetrachlorohexafluorocyclopentane with zinc dust in dioxan, shows indications of being as reactive and versatile as its hydrocarbon and chlorocarbon analogues in its reactions with dienophiles, metal carbonyls, etc.[1]

Fluorination of perchlorocyclopentadiene with cobalt trifluoride gave tetrachlorohexafluorocyclopentane in *ca.* 33% yield; no attempt was made to separate the geometrical isomers that were doubtless present.

Perfluorocyclopentadiene is a colourless liquid, which has a strong C=C stretching vibration at 1770 cm.$^{-1}$ (spectrum of vapour) and absorbs (spectrum of vapour) at 268 mμ ($\lambda_{\max.}$, $\varepsilon = 850$; $\lambda_{\min.}$ 205 mμ, $\varepsilon = 265$). It dimerises at room temperature. Chlorination yields 1,2,3,4-tetrachlorohexafluorocyclopentane, and permanganate oxidation converts it into a mixture of oxalic and difluoromalonic acids.

Experimental

Analytically pure perchlorocyclopentadiene, b. p. 106°/14 mm., was obtained by distillation of a commercial sample. Since perfluorocyclopentadiene is volatile and susceptible to attack by moist air, it was manipulated in a conventional Pyrex vacuum system.

Fluorination of Perchlorocyclopentadiene with Cobalt Trifluoride.—(a) *Apparatus.* Three horizontal reactors (A, B, and C) containing cobalt trifluoride were used. Reactor A was an electrically heated mild-steel tube (24 in. long × 2 in. i.d.) containing a copper tray filled with cobalt trifluoride (300 g.; available fluorine, 50 g.), into which perchlorocyclopentadiene was fed *via* a liquid seal and an electrically heated vaporiser; the fluorination products were collected in two Pyrex traps cooled to 0° and $-72°$, respectively. Reactor B (4 ft. long × 4·5 in. i.d.) was equipped with metal traps; it contained 1,900 g. (available fluorine, 310 g.) of cobalt trifluoride divided between four copper trays stacked in pairs. Temperatures in both A and B were measured by chromel–alumel thermocouples placed in mild-steel pockets that extended vertically from the tops of the reactor tubes into the beds of cobalt trifluoride. Reactor C was a gas-heated copper pipe (51 in. × 4·5 in.) equipped with a coaxial nickel stirrer to agitate the cobalt trifluoride (~7 kg.; available fluorine, ~1·2 kg.); the nickel stirrer had a hollow shaft to accommodate chromel–alumel thermocouples.

(b) *Operation.* Standard techniques were used to operate the reactors, but it was necessary to purge them with a brisk stream of nitrogen for 4—6 hr. at the end of each experiment to ensure complete removal of the products into the traps. During this operation, the line leading into the first trap was heated intermittently to prevent solidification of products. The contents of the traps were stirred with an excess of aqueous sodium hydrogen carbonate solution, then washed with water, and dried ($CaCl_2$).

(c) *Results.* Perchlorocyclopentadiene (25·5 g.) was fed into reactor A at 190—200° during 30 min. The product (10·0 g.) was analysed by gas–liquid chromatography (g.l.c.) (column: 1 m., Apiezon L–Celite; 160°; nitrogen flow-rate, 35 ml./min.); it contained two major components (retention times, 2·2 min. and 6·0 min.) and about four minor components. The major components were isolated by large-scale gas chromatography (column: 6 m. × 3 m. silicone MS 550–Celite; 150°; nitrogen flow-rate, 300 ml. min.) and found to be a tetrachlorohexafluorocyclopentane fraction (Found: C, 19·0; Cl, 44·7; F, 36·1%; *M*, 317. Calc. for $C_5Cl_4F_6$: C, 19·0; Cl, 44·9; F, 36·1%; *M*, 316), m. p. *ca.* 28°, b. p. (micro) 150—151°, n_D^{20}

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[1] Banks, Harrison, Haszeldine, Lever, and Smith, unpublished results.

(super-cooled liquid) 1·4061, and a pentachloropentafluorocyclopentane fraction (Found: Cl, 53·3; F, 28·0. Calc. for $C_5Cl_5F_5$: Cl, 53·3; F, 28·6%), b. p. 120°/100 mm.

To obtain sufficient tetrachlorohexafluorocyclopentane for dechlorination studies, a series of fluorinations was carried out in reactor B and in reactor C. The effect of conditions on the yield of tetrachlorohexafluorocyclopentane was approximately determined by separating the product from each experiment into four fractions with boiling ranges 60—145°, 145—165°, 165—185°, and >185° by distillation (30 cm. × 1·5 cm.; column packed with 2·2 mm. Fenske glass rings). The second fraction was shown by g.l.c. analysis to be mainly (>80%) the required halogenocyclopentane, and its weight was greatest when the reactors were operated under the following conditions [reactor, temp., rate of addition of C_5Cl_6 (ml./min.), available F used (%)]: B, 200—220°, 1·4, 17; C, 150—220°, 5·0, 65. Under these optimum conditions an estimated yield of 33% of tetrachlorohexafluorocyclopentane was obtained with both reactors.

A total of 10·1 kg. of perchlorocyclopentadiene was fluorinated to yield 7·05 kg. of product, which was separated into four fractions as described above; the first three fractions were redistilled (30 cm. × 8 mm. Podbielniak column packed with Nichrome Heli-pak or 60 cm. × 1 cm. column packed with stainless steel $\frac{1}{16}$ in. × $\frac{1}{16}$ in. Dixon rings), to yield the following materials: a trichloroheptafluorocyclopentane fraction (394 g.) (Found: C, 20·0; Cl, 35·1; F, 44·7%; *M*, 301. Calc. for $C_5Cl_3F_7$: C, 20·0; Cl, 35·6; F, 44·4%; *M*, 299·5), b. p. 114—116°, $n_D^{20\cdot4}$ 1·3724, d_4^{20} 1·76, tetrachlorohexafluorocyclopentane (1185 g.), b. p. 150—151°; and pentachloropentafluorocyclopentane (2100 g.), b. p. 115°/95 mm.

Preparation of Perfluorocyclopentadiene.—Tetrachlorohexafluorocyclopentane (64·0 g., 0·20 mole) in dioxan (10 ml.) was added to a stirred suspension of activated zinc dust (80 g., 1·2 moles) in refluxing dioxan (100 ml.), and the mixture was refluxed for 2 hr., the vessel being swept with a slow stream of nitrogen with the water condenser kept at 40°. The volatile product, collected in two traps cooled to −72° and −196°, respectively, was distilled [15 cm. × 1 cm. i.d. column packed with Heli-pak Hastelloy B wire coils (0·05 × 0·10 × 0·10 in.)] to yield *perfluorocyclopentadiene* (15·5 g., 0·09 mole; 44%) (Found: C, 34·4%; *M*, 174. C_5F_6 requires C, 34·5%; *M*, 174), b. p. 28°, with a retention time of 2·1 min. on a 1-m. Kel-F 40–Celite column at 22° (nitrogen flow-rate, 24 ml. min.).

The zinc dust was activated by stirring it for approximately 4 min. with 2N-hydrochloric acid; it was then washed several times with distilled water, thoroughly dried in a vacuum, and then stored before use in sealed Polythene bags containing an atmosphere of nitrogen. Attempts to prepare perfluorocyclopentadiene by dechlorination of tetrachlorohexafluorocyclopentane with activated zinc dust in ethanol or n-butanol resulted either in failure or a variable yield (1—23%) of material contaminated by hydrogen-containing compounds which could not be removed by distillation.

Reactions of Perfluorocyclopentadiene.—(a) *Dimerisation* (with A. C. Harrison). When a freshly-distilled sample (1·5 g., 8·6 mmoles) of perfluorocyclopentadiene was stored *in vacuo* at room temperature it was 80% converted into a *dimer* (1·2 g.) during 14 days (Found: C, 34·8%; *M*, 340. $C_{10}F_{12}$ requires C, 34·5%; *M*, 348), subl. 25°/10 mm., m. p. 42·5—43°. A melt showed C=C absorption at 1748 cm.$^{-1}$.

Dimerisation (26%) occurred even at −10° during 24 hr., so it was stored at −196° *in vacuo* immediately after isolation.

(b) *Oxidation.* (i) Perfluorocyclopentadiene (0·59 g., 3·4 mmoles) in diethyl ether (10 ml.) was added to a stirred solution of potassium permanganate (1·5 g.) in acetone (100 ml.); manganese dioxide was precipitated. Water (100 ml.) was added, the solution neutralised with sodium hydrogen carbonate, and acetone removed *in vacuo*. The remaining solution was decolorised with sulphur dioxide and evaporated to dryness. The residue was sublimed and the sublimate treated, in ethereal solution, with aniline. The dianilinium salt was crystallised from acetone–chloroform to yield dianilinium difluoromalonate (0·32 g., 0·80 mmole; 24%) (Found: C, 55·1; H, 4·7; N, 8·8%; Equiv., 158. Calc. for $C_{15}H_{16}F_2N_2O_4$: C, 55·2; H, 4·9; N, 8·6%; Equiv., 163), m. p. 160—162° (lit.,[2] 160—161°).

(ii) Perfluorocyclopentadiene (0·65 g., 3·7 mmoles) was shaken with a solution of potassium permanganate (1·4 g.) in acetone (100 ml.) for 1 hr. The product was worked up as before, but, after sulphur dioxide had been passed, the solution was boiled and made just alkaline, and calcium chloride solution was added. The precipitate was extracted with 2N-hydrochloric

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[2] Evans and Tatlow, *J.*, 1954, 3779.

acid and the extract (pH adjusted to 4) was added to a solution of *S*-benzylthiouronium chloride to give di-(*S*-benzylthiouronium) oxalate (0·091 g., 0·21 mmole, 6%) (Found: C, 51·2; H, 5·1; N, 13·1. Calc. for $C_{18}H_{22}N_4O_4S_2$: C, 51·0; H, 5·2; N, 13·3%), m. p. 198—200°, mixed m. p. 197—199°.

(c) *Chlorination.* Perfluorocyclopentadiene (0·125 g., 0·72 mmole) and an excess of redistilled chlorine (0·280 g., 4·00 mmoles) were kept in a Pyrex ampoule at room temperature for 2 days. The unchanged chlorine (0·156 g., 2·20 mmoles, 54%) was measured. The liquid product (0·21 g., 0·66 mmole, 92%) recovered from the tube was 1,2,3,4-tetrachlorohexafluorocyclopentane contaminated with about 5% of an unknown compound (by g.l.c. analysis).

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