[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

Chlorination of Fluorine-containing Alcohols[1]

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The chlorination of four fluorine-containing alcohols in an inert solvent was studied. 2,2,3,3,4,4,4-Heptafluoro-1-butanol yielded heptafluorobutanal, while 3,3,4,4,5,5,5-heptafluoro-2-pentanol gave 3,3,4,4,5,5,5-heptafluoro-2-pentanone. Chlorination of 4,4,5,5,6,6,6-heptafluoro-3-hexanol produced the two isomeric chlorohydrins and a trace of 4,4,5,5,6,6,6-heptafluoro-3-hexanone. The tertiary alcohol, 3,3,4,4,5,5,5-heptafluoro-2-methyl-2-pentanol formed the chlorohydrin which was converted to the corresponding epoxide.

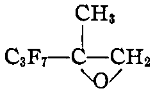
Discussion

The chlorination of fluorine-containing alcohols using elemental chlorine in an inert solvent was studied as a means of preparing chlorohydrins for use in the synthesis of glycols and epoxides.

The initial experiments were conducted with 3,3,4,4,5,5,5-heptafluoro-2-pentanol which yielded only the corresponding ketone, 3,3,4,4,5,5,5-heptafluoro-2-pentanone. Consequently, the alcohol 2,2,3,3,4,4,4-heptafluoro-1-butanol was chlorinated and found to give only heptafluorobutyraldehyde. It is presumed that these reactions are analogous to that described for the preparation of chloral by chlorination of ethanol[2] in which a hypochlorite intermediate is formed which decomposes under the conditions of the reaction to form the carbonyl group.

TABLE I

NEW COMPOUNDS

Compound	B.p., °C. at 745 mm.	M.p., °C.	n^{20}_D	d^{20}_4	Carbon, % Found	Carbon, % Calcd.	Hydrogen, % Found	Hydrogen, % Calcd.
$C_3F_7CHOHC_2H_5$	113.5	−14	1.3255	1.439	31.8	31.6	3.20	3.10
$C_3F_7COH(C_2H_5)_2$	142	−12	1.3526	1.295	37.4	37.5	4.40	4.30
$C_3F_7COCH_3$	63.5	76.5[a]	1.3000	1.424	28.1	28.3	1.43	1.42
$C_3F_7CHOHCH_2CH_2Cl$	156	11–12	1.3560	1.558	27.4	27.5	2.20	1.90
$C_3F_7CHOHCH_2CH_2OH$		90–91			29.0	29.5	2.95	2.87
$C_3F_7COH(CH_3)(CH_2Cl)$	129	− 2	1.3553	1.559	27.5	27.5	2.45	2.24
 $C_3F_7-\overset{CH_3}{\overset{\vert}{C}}-CH_2$ (epoxide, $\underset{O}{\smile}$)	93	−70	1.3107	1.391	31.6	31.8	2.43	2.20

[a] M.p. of 2,4-dinitrophenylhydrazone.

In contrast to the previous reactions, the chlorination of 4,4,5,5,6,6,6-heptafluoro-3-hexanol resulted in the formation of only a trace of the corresponding ketone. The principal products were the two chlorohydrins, 1-chloro-4,4,5,5,6,6,6-heptafluoro-3-hexanol and 2-chloro-4,4,5,5,6,6,6-heptafluoro-3-hexanol. These were identified by first converting them to the corresponding glycols with aqueous potassium carbonate followed by reaction with periodic acid.

The tertiary alcohol, 3,3,4,4,5,5,5-heptafluoro-2-methyl-2-pentanol, was chlorinated to form the chlorohydrin, 1-chloro-3,3,4,4,5,5,5-heptafluoro-2-methyl-2-pentanol, and a mixture of the isomeric dichloro derivatives. The chlorohydrin formed the corresponding epoxide on treatment with 20% sodium hydroxide at 100°.

The new compounds prepared, their physical properties and analyses are given in Table I.

Experimental

Starting Materials.—(a) 2,2,3,3,4,4,4-Heptafluoro-1-butanol was prepared by reduction of heptafluorobutyryl chloride with lithium aluminum hydride.[3] (b) 3,3,4,4,5,5,5-Heptafluoro-2-pentanol was prepared by reaction of heptabutyraldehyde with methylmagnesium iodide.[4] (c) 3,3,4,4,5,5,5-Heptafluoro-2-methyl-2-pentanol was prepared by reaction of methyl heptafluorobutyrate with methylmagnesium bromide.[5] (d) 4,4,5,5,6,6,6-Heptafluoro-3-hexanol was prepared as follows: A solution of 228 g. (1 mole) of methyl heptafluorobutyrate in 500 ml. of dry ether was added to 3 moles of ethylmagnesium bromide contained in a 5-liter, 3-necked flask fitted with a mercury-sealed stirrer, a dropping funnel and a reflux condenser. The mixture was allowed to stand overnight and then hydrolyzed with dilute sulfuric acid. The ether layer was dried and the product fractionated to yield 127 g. (0.56 mole) of 4,4,5,5,6,6,6-heptafluoro-3-hexanol and 26 g. (0.10 mole) of 3-ethyl-4,4,5,5,6,6,6-heptafluoro-3-hexanol. The yield of the secondary alcohol was 56% and the yield of the tertiary alcohol was 10%. A similar reduction reaction was observed by Campbell.[6]

Chlorination Procedure.—A solution of 1 volume of the fluorine-containing alcohol and 2 volumes of carbon tetrachloride was placed in a 500-cc. Pyrex test-tube. Chlorine was admitted through a fritted glass disk reaching to the bottom of the tube and the exit gases passed through a reflux condenser and then through a Dry Ice cooled trap before going through a water scrubbing tower. The bottom of the chlorination tube was wound with resistance wire for heating purposes. The mixture was heated to 60° and the chlorine passed in through a sulfuric acid bubbler at a rapid rate. Illumination was provided by a mercury vapor light and a 300 watt bulb. After initiation of the reaction, heating was discontinued and chlorine was passed into the solution until chlorine was obtained in the Dry Ice cooled trap.

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[1] This paper represents part of a thesis submitted by W. F. Marzluff to the Graduate School, Purdue University, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] N. V. Sidgwick, "The Chemical Elements and their Compounds," Vol. II, Oxford University Press, London, 1950, p. 1218.

(3) Minnesota Mining and Manufacturing Company, "Fluorochemicals," 1949.

(4) E. T. McBee, O. R. Pierce and J. F. Higgins, THIS JOURNAL, **74**, 1736 (1952).

(5) E. T. McBee, O. R. Pierce and M. C. Chen, *ibid.*, **75**, may (1953).

(6) K. N. Campbell, J. O. Knoblock and B. H. Campbell, *ibid.*, **72**, 4380 (1950).

The chlorine was stopped, and air blown through the reaction mixture for 0.5 hour to remove dissolved chlorine and hydrogen chloride. The chlorine was distilled from the Dry Ice cooled trap and any high boiling residue was returned to the reaction mixture. The reaction mixture was then rectified on a Todd precision fractionating assembly. When all the solvent was removed, rectification was continued at reduced pressure. This procedure was followed in each of the cases described.

2,2,3,3,4,4,4-Heptafluoro-1-butanol Chlorination.—Forty-three grams of 2,2,3,3,4,4,4-heptafluoro-1-butanol in carbon tetrachloride was treated with chlorine for 2 hours. Ice-water was passed through the reflux condenser. The reaction mixture was distilled to yield 10 g. of heptafluorobutanal boiling at 29° at 745 mm. pressure, and 24 g. of unreacted alcohol or a yield of 80% and a conversion of 24%.

Chlorination of 3,3,4,4,5,5,5-Heptafluoro-2-pentanol.—Sixty-seven grams (0.31 mole) of 3,3,4,4,5,5,5-heptafluoro-2-pentanol in carbon tetrachloride was chlorinated for 2 hours and fractionation of the resulting mixture resulted in 63 g. of a product boiling at 60° at 745 mm. pressure, which was an azeotrope of 3,3,4,4,5,5,5-heptafluoro-2-pentanone and carbon tetrachloride. The 2,4-dinitrophenylhydrazone of the ketone was prepared, m.p. 76–76.5°.

Anal. Calcd. for $C_{11}H_7F_7O_4N_4$: N, 14.30. Found: N, 14.47.

The 2,4-dinitrophenylhydrazone was hydrolyzed with concentrated sulfuric acid and the pure ketone isolated, boiling at 63.5° at 740 mm. The yield was 70%.

4,4,5,5,6,6,6-Heptafluoro-3-hexanol.—Sixty-four grams of 4,4,5,5,6,6,6-heptafluoro-3-hexanol in 88.5 g. of carbon tetrachloride was chlorinated as previously described. The reaction time was 2.5 hours. The fraction boiling at 70–74° during rectification was identified as a mixture of 4,4,5,5,6,6,6-heptafluoro-3-hexanone and carbon tetrachloride, by means of the 2,4-dinitrophenylhydrazone, m.p. 70–71°.

Anal. Calcd. for $C_{12}H_9F_7O_4N_4$: N, 13.80. Found: N, 13.70,

Fractions boiling over the range 135–156° were monochloro alcohols, isomers of the general formula $C_3F_7CHOHC_2H_4Cl$. The monochloroalcohols were combined and rectified to yield two main fractions, alcohol (I) b.p. 136–140° at 745 mm. pressure (with decomposition), alcohol (II) b.p. 156° at 745 mm. pressure (68% yield).

Alcohols (I) and (II) were each refluxed for 24 hours with 10 g. of potassium carbonate in 50 ml. of water. The lower organic layers were separated, the water layers, containing much chloride ion, were extracted with ether, the ether extract combined with the organic layer and the mixture dried over Drierite. The dried extracts were distilled at atmospheric pressure. Alcohol (II) yielded, besides unreacted starting material, a chlorine-free solid, m.p. 90-91° after recrystallization from benzene. This solid gave a negative test with periodic acid even after heating, and was therefore identified as 4,4,5,5,6,6,6-heptafluoro-1,3-hexanediol.

The distillation of the hydrolysis product of alcohol (I) did not yield a product completely free of chlorine, but a high boiling liquid, b.p. 170–175°, was obtained. It did not give a positive test with silver nitrate solution but did give a positive periodic acid test. On the basis of these results, the chlorohydrins (I) and (II) were assigned the following structures: $C_3F_7CHOHCHClCH_3$ (I), $C_3F_7CHOHCH_2CH_2Cl$ (II).

Chlorination of 3,3,4,4,5,5,5-Heptafluoro-2-methyl-2-pentanol.—A solution of 100 g. (0.44 mole) of 3,3,4,4,5,5,5-heptafluoro-2-methyl-2-pentanol in carbon tetrachloride was treated with chlorine for 5 hours. Fractionation of the products gave 43.1 g. (0.16 mole) of 1-chloro-3,3,4,4,5,5,5 heptafluoro-2-methyl-2-pentanol (37% yield) and 37.5 g. of the dichloro compound.

1,2-Epoxy-3,3,4,4,5,5,5-heptafluoro-2-methylpentane.—Thirty-nine grams of 1-chloro-3,3,4,4,5,5,5-heptafluoro-2-methyl-2-pentanol was added slowly through a dropping funnel to 50 g. of a 20% sodium hydroxide solution in a distilling flask maintained at 100°. When half of the chlorohydrin had been added, a liquid began steam distilling from the mixture. The distillation began at 78° and was continued until no more organic material was evident in the distillate. The water layer in the distillate was separated and the crude product was dried over Drierite. The product was rectified and 32.1 g. (93% yield) of 1,2-epoxy-3,3,4,4,5,5,5-heptafluoro-2-methylpentane was obtained.

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LAFAYETTE, INDIANA

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Electron Exchange-Polymers. III. Polymers and Copolymers of Vinylhydroquinone

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The preparation and properties of vinylhydroquinone dibenzoate and diacetate, of polyvinylhydroquinone, and copolymers of the dibenzoate and of the free hydroquinone with styrene, with α-methylstyrene, with vinyl pyridine; and with styrene, cross-linked with divinylbenzene are described. The oxidation behaviors of some of these substances are shown and discussed. It is established that high polymers capable of showing oxidation–reduction properties have been prepared, and some physical and chemical properties of these substances are discussed.

In this paper are reported the preparation and properties of polyvinylhydroquinone and copolymers with styrene, α-methylstyrene, vinylpyridine and styrene and divinylbenzene.

In previous reports the concept of the electron exchange-polymer ("redox resin") was presented[1] and the preparation of vinylhydroquinone and its polymerization by heat were described.[2] Titration curves for the oxidation of the product of this polymerization alone, in suspension, and dispersed in the presence of bovine serum albumin were reported. While it turned out that the polymerized vinylhydroquinone prepared in this way was of low molecular weight (corresponding largely to the dimer and trimer) the oxidation findings as well as the general discussions of the experimental work[1,2] are supported by the results obtained with high polymer and reported here. This is because the low molecular weight material "polymerized vinylhydroquinone" is quite insoluble in aqueous solvents, so that over at least part of the titration curves in such solvents a heterogeneous system was present (precipitation occurred) and because, also, the substance contained a range of molecular sizes, and at least two chemical groupings with different oxidizabilities.[3] Nevertheless, these re-

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[1] H. G. Cassidy, THIS JOURNAL, **71**, 402 (1949).

[2] I. H. Updegraff and H. G. Cassidy, *ibid.*, **71**, 407 (1949).

[3] I. H. Updegraff and H. G. Cassidy, presented before the Organic Division at the Philadelphia Meeting of the American Chemical Society, April, 1950.