methanol was treated with 10 ml. of 70% sulfuric acid–methanol solution. After being thoroughly mixed the solution was left at room temperature for 2 hr. and then poured into 50 ml. of ice water. The resulting mixture was stirred until the product solidified. The solid material was collected on a filter and washed free of acid. The β-nitro alcohol weighed 2.4 g. and melted at 101–103°. One recrystallization from benzene–hexane gave 2.0 g. (83%) of *threo*-1,2-diphenyl-2-nitro-1-ethanol, m.p. 103.5–104°; reported, 106–107°.[6]

A sample of the β-nitro alcohol was recovered after treatment with hot 20% sulfuric acid–dioxane for 20 min. Similar treatment of 1,2-diphenylethanol afforded an 87% yield of *trans*-stilbene, m.p. 121.5–122.5°. (This experiment illustrates the retarding effect of the nitro group on the rate of dehydration.)

***cis*-α-Nitrostilbene.**—A sample (0.50 g.) of *threo*-1-acetoxy-1,2-diphenyl-2-nitroethane dissolved in 5 ml. of dimethylformamide was treated with a trace of sodium nitrite. The mixture was stirred for 25 min. at room temperature and then treated with water. A quantitative yield (0.39 g.) of crude α-nitrostilbene, m.p. 68–70°, was obtained. Recrystallization from hexane raised the melting point to 72–73°, reported m.p. 74–75°.[7] A comparable result was obtained using triethylamine in dioxane.

***cis*-Stilbene and Acetyl Nitrate.**—*cis*-Stilbene, 15 g. (0.082 mole) was treated with a nitration mixture of 7.3 g. (0.082 mole) of nitric acid and 150 ml. of acetic anhydride, at 0° for 1 hr. and at 15° for 14 hr. The semisolid obtained after hydrolysis of the excess acetic anhydride was separated and digested with 25 ml. of methanol at 0° for 15 min. A total of 11.5 g. (48%) of crude *threo*-1-acetoxy-1,2-diphenyl-2-nitroethane, m.p. 129–133°, was obtained by filtration. The methanol filtrate released 8.0 g. of yellow oil on further dilution with water. The oil exhibited strong infrared maxima at 6.05 μ, 7.83 μ, and 11.9 μ, indicating the presence of a large proportion of β-nitro nitrate.[22] Somewhat weaker absorptions characteristic of β-nitro acetate and nitroalkene were also apparent.

In a second experiment, 4.5 g. (0.025 mole) of *cis*-stilbene was nitrated as described in the general nitration procedure using 4.5 g. (0.05 mole) of nitric acid, 30 ml. of acetic anhydride, and 1 drop of sulfuric acid. There was little evidence of reaction at −15°, and the nitration mixture was allowed to warm to 10° over a period of 15 min. before quenching in water. The infrared spectrum of the crude oily nitration products indicated a large proportion of β-nitro nitrate. The nitration products were chromatographed as for *trans*-stilbene to afford 1.53 g. (34%) of unchanged alkene (1.30 g. of mostly *cis*-stilbene and 0.23 g. of mostly *trans*-stilbene) and 1.47 g. (21%) of crude *threo*-β-nitro acetate, m.p. 120–130°. One recrystallization of the latter from methanol gave 1.23 g. of the *threo* isomer, m.p. 132–134°. Additional fractions were oils and did not lend themselves to specific characterization.

***trans*-α-Methylstilbene and Acetyl Nitrate.**—*trans*-α-Methylstilbene, 9.7 g. (0.05 mole), was nitrated following the general nitration procedure and using 9.0 g. (0.10 mole) of nitric acid, 70 ml. of acetic anhydride, and 2 drops of sulfuric acid. After addition of the finely powdered alkene to the nitration mixture at −15°, the reaction mixture was allowed to warm to 10° before quenching in water. The oily product was digested with 30 ml. of methanol at 0°, and the resulting solid was collected by filtration. After washing with 10 ml. of cold methanol, 6.2 g. (41%) *threo*-1,2-diphenyl-1-nitro-2-acetoxypropane, m.p. 103.5–104.5°, was obtained; reported, m.p. 106°.[5]

***cis*-α-Methylstilbene and Acetyl Nitrate.**—Using the general nitration procedure, 1.9 g. (0.01 mole) of *cis*-α-methylstilbene (dissolved in 6 ml. of acetic anhydride) was nitrated with 1.8 g. (0.02 mole) of nitric acid, 12 ml. of acetic anhydride, and 1 drop of sulfuric acid. After hydrolysis of the excess acetic anhydride, the product was extracted with benzene. The benzene layer was washed thoroughly, dried over sodium sulfate, and stripped under reduced pressure. The infrared spectrum of the residual oil revealed the presence of only a trace of nitrate ester. Essentially equal intensity unconjugated and conjugated nitro peaks were present. The oil was dissolved in a minimum amount of benzene and the solution placed on a 2.5 × 30-cm. silica gel column slurry packed with 40% (by volume) benzene in hexane. Successive elutions with 40% benzene in hexane (200 ml.), 60% benzene in hexane (500 ml.), and benzene (950 ml.) gave fractions containing 0.75 g. of an oily mixture of conjugated and unconjugated nitroalkenes (by infrared inspection) and 0.77 g. (26%) of oily β-nitro acetate; the infrared spectrum of the latter was practically identical with that of the *threo*-1,2-diphenyl-1-nitro-2-acetoxypropane. After seeding with a sample of the *threo* isomer and recrystallization from methanol, 0.43 g. of the *threo*-β-nitro acetate,[5] m.p. 104–105°, was obtained, together with 0.33 g. of oil which could not be induced to crystallize.

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[22] J. F. Brown, Jr., *J. Am. Chem. Soc.*, **77**, 6341 (1955).

The Radiation-Induced Addition Reaction of Alcohols to Perhalogeno Olefins

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The radiation-induced addition reactions of alcohols to perhalogeno olefins such as 1-fluoro-1,2,2-trichloroethylene, 1,2-difluoro-1,2-dichloroethylene, and 1,1-difluoro-2,2-dichloroethylene were carried out. While the addition of alcohols to 1-fluoro-1,2,2-trichloroethylene and 1,2-difluoro-1,2-dichloroethylene gave mainly 1:1 adducts in appreciable yields, 1,1-difluoro-2,2-dichloroethylene reacted with alcohols to give telomers. The direction of addition of α-hydroxyalkyl radicals to the olefins was determined.

Since Urry and co-workers[1] have shown that alcohols added to olefins by peroxide- and light-induced reactions, a number of reports[2] concerning the addition of alcohols to olefins have been

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[1] W. H. Urry, F. W. Stacey, E. S. Huyser, and O. O. Juveland, *J. Am. Chem. Soc.*, **76**, 450 (1954).

[2] C. Walling, "Free Radicals in Solution," J. Wiley & Sons, Inc., New York, N. Y., 1957, p. 285.

TABLE I

HALOGENO ALCOHOLS (1:1 ADDUCTS)

							MRD		Fluorine, %		Chlorine, %	
R_1	R_2	Yield, %	B.p.	Mm.	n^{20}_D	d^{20}_4	Calcd.[a]	Found	Calcd.	Found	Calcd.	Found
						$CHCl_2CFClCR_1R_2OH$						
H	H	13	88–89	20	1.4694	1.583	32.26	31.94	10.47	10.79	58.63	58.31
CH_3	H	67	74–75	10	1.4700	1.495	36.88	36.48	9.72	9.90	54.42	54.08
C_2H_5	H	42	82–84	10	1.4707	1.424	41.50	41.01	9.07	9.29	50.78	50.19
CH_3	CH_3	60	79–81	10	1.4727	1.439	41.50	40.82	9.07	9.29	50.78	50.41
						$CHFClCFClCR_1R_2OH$						
H	H	16	76–77	40	1.4230	1.536	27.47	27.35	23.03	22.83	42.99	42.19
CH_3	H	40	68–69	20	1.4292	1.460	32.09	31.61	21.22	21.21	39.61	39.48
C_2H_5	H	43	78–80	20	1.4330	1.384	36.71	36.25	19.69	19.82	36.74	36.28
CH_3	CH_3	86	73–74	20	1.4350	1.393	36.71	36.16	19.69	19.48	36.74	36.78
						$CHCl_2CF_2CR_1R_2OH$						
H	H	4	81–82	40	1.4241	1.556	27.47	27.06	23.03	23.20	42.99	42.55
CH_3	H	10	74–76	20	1.4270	1.465	32.09	31.37	21.22	21.10	39.61	38.91
C_2H_5	H	10	84–86	20	1.4299	1.393	36.71	35.79	19.69	19.48	36.74	36.25
CH_3	CH_3	15	81–82	20	1.4355	1.401	36.71	36.00	19.69	19.87	36.74	36.89

[a] Molecular refractions calculated by adding the customary increments of the pertinent elements AR_F [1,13].

presented, and the free radical addition reactions for the preparation of fluorine-containing alcohols have received considerable attention.

Joyce[3] reported in his patent that alcohols such as methanol, ethanol, propanol-1, and propanol-2 added to tetrafluoroethylene to form telomers, for example, $H(CF_2\text{-}CF_2)_nCH_2OH$ (n = 1–12). LaZerte and Koshar[4] have obtained 1:1 adducts in the free radical reactions of alcohols to perfluoropropene, perfluorobutene-1, and perfluorobutene-2. Park, and co-workers[5] have found a variety of perhaloalkanes to react with both allyl and propargyl alcohols in a photochemical reaction or in the presence of peroxide.

The present work deals with the γ-radiation induced addition reaction of alcohols to perhalogeno olefins such as 1-fluoro-1,2,2-trichloroethylene, 1,2-difluoro-1,2-dichloroethylene, and 1,1-difluoro-2,2-dichloroethylene. The general reaction is

$$CHR_1R_2OH + CFX{=}CX_2 \longrightarrow CHX_2CFXCR_1R_2OH$$

$$X = F \text{ or } Cl;\ R_1 = H \text{ or } CH_3;\ R_2 = H,\ CH_3, \text{ or } C_2H_5$$

In preliminary experiments, benzoyl peroxide was found to be effective for the addition reaction, but benzoates of alcohols were produced as byproducts whose boiling products were similar to the 1:1 adducts. The γ-radiation induced addition reaction of 1-fluoro-1,2,2-trichloroethylene and 1,2-difluoro-1,2-dichloroethylene gave mainly 1:1 adducts in appreciable yields. 1,1-Difluoro-2,2-dichloroethylene reacted with alcohols under the influence of γ-radiation to form telomers.

The reactants were irradiated in a glass tube at a rate of 0.8×10^5 röntgens per hour for a period of two weeks in most instances. The 1:1 adducts were thought to be formed by the addition of α-hydroxyalkyl radicals to the halogenoölefins by the mechanism of Urry and co-workers,[1] for example

$$CH_3CH_2OH \xrightarrow{\gamma\text{-ray}} CH_3\dot{C}HOH + H\cdot$$

$$CH_3\dot{C}HOH + CF_2{=}CCl_2 \longrightarrow \dot{C}Cl_2CF_2C(CH_3)HOH$$

$$\dot{C}Cl_2CF_2C(CH_3)HOH + CH_3CH_2OH \longrightarrow$$
$$CHCl_2CF_2C(CH_3)HOH + CH_3\dot{C}HOH$$

The yields and physical properties of the 1:1 adducts, the new halogeno alcohols, are shown in Table I. Table II shows the 1:2 adducts of alcohols to 1,1-difluoro-2,2-dichloroethylene.

The trend in gross reactivity observed in the addition of alcohols to 1,2-difluoro-1,2-dichloroethylene is as follows

$$(CH_3)_2CHOH > CH_3(CH_2)_2OH,\ CH_3CH_2OH > CH_3OH$$

This order of reactivity of alcohols is consistent with the apparent stabilization of α-hydroxyalkyl radicals which is due to their resonance. In the addition of alcohols to 1-fluoro-1,2,2-trichloroethylene, however, the yield of 1:1 adduct of ethanol was better than those of propanol-1 and propanol-2. The similar trend was also reported by Yumoto and Matsuda[6] in the γ-radiation induced addition reaction of alcohols to tetrachloroethylene.

Decrease of reactivity of propanol-2 in the additions to 1-fluoro-1,2,2-trichloroethylene and tetrachloroethylene would be due to the steric interference of the bulky chlorine atoms in the olefins.

The chemical reactions were used in order to determine the direction of the additions of α-hydroxyalkyl radicals formed to 1-fluoro-1,2,2-trichloroethylene and 1,1-difluoro-2,2-dichloroethylene. Oxidation of the 1:1 adducts of methanol to the olefins gave the corresponding fluorochloro acids. Pyrolyses of the sodium salts of these acids

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(3) R. M. Joyce (to Du Pont), U.S. Patent 2,559,628 (July 10, 1951).

(4) J. D. LaZerte and R. J. Koshar, *J. Am. Chem. Soc.*, **77**, 910 (1955).

(5) J. D. Park, F. E. Rogers, and J. R. Lacher, *J. Org. Chem.*, **26**, 2089 (1961).

(6) K. Yumoto and T. Matsuda, Abstract, Symposium on Organic Synthesis by Free-Radical Reactions, Osaka, Japan (1961).

TABLE II

HALOGENO ALCOHOLS (1:2 ADDUCTS), $H(CCl_2CF_2)_2CR_1R_2OH$[a]

		Yield,					MRD		Fluorine, %		Chlorine, %	
R_1	R_2	%	B.p.	Mm.	$n^{20}D$	d^{20}_4	Calcd.[a]	Found	Calcd.	Found	Calcd.	Found
H	H	2	85–90	17	1.4513	1.772	46.60	45.29	25.51	25.03	47.61	45.23
CH_3	H	2	95–98	8	1.4350	1.541	51.22	52.82	24.36	23.40	45.47	42.68
C_2H_5	H	4	100–103	9	1.4368	1.468	55.84	58.15	23.32	21.96	43.51	39.63
CH_3	CH_3	7	96–98	8	1.4582	1.605	55.84	55.44	23.32	23.86	43.51	44.15

[a] No rectification.

TABLE III

HALOGENOBUTENES

				MRD		Fluorine, %		Chlorine, %	
Compounds	B.p.	$n^{20}D$	d^{20}_4	Calcd.	Found	Calcd.	Found	Calcd.	Found
$CHCl_2CFClC(CH_3){=}CH_2$	164–166	1.4733	1.348	39.50	39.87	9.92	9.32	55.55	55.88
$CHFClCFClC(CH_3){=}CH_2$	127–129	1.4282	1.295	34.72	34.79	21.71	21.13	40.52	40.82
$CHCl_2CF_2C(CH_3){=}CH_2$	130–131	1.4245	1.306	34.72	34.23	21.71	21.85	40.52	40.13
$CHCl_2CFClCH{=}CH_2$[a]	129–132	1.4650	1.364			10.71	7.14	59.95	58.04
$CHCl_2CF_2CH{=}CH_2$	100–101	1.4170	1.325	30.10	30.55	23.60	22.52	44.05	43.52

[a] Crude sample.

resulted in 1,2-dichloro-1-fluoroethylene and 1-chloro-2,2-difluoroethylene, respectively.

$$CHCl_2CFClCH_2OH \xrightarrow[\text{2. aq. NaOH}]{\text{1. } K_2Cr_2O_7} CHCl_2CFClCOONa \xrightarrow{\Delta} CHCl{=}CFCl + NaCl + CO_2$$

$$CHCl_2CF_2CH_2OH \longrightarrow CHCl_2CF_2COONa \longrightarrow CHCl{=}CF_2 + NaCl + CO_2$$

The structures of the olefins produced by pyrolyses were determined by comparing their infrared spectra with those of the authentic olefins[7] prepared by the procedure of Henne and co-worker.[8] Thus, it was found that the α-hydroxyalkyl radicals add to the $=CFCl$ side in 1-fluoro-1,2,2-trichloroethylene and to the $=CF_2$ side in 1,1-difluoro-2,2-dichloroethylene. These results confirm the general rule for the addition of radicals to the olefins, that is, that the radicals add to the side having less steric hindrance.[9]

It was observed that the boiling points of all 1:1 adducts of 1,1-difluoro-2,2-dichloroethylene are higher by about 6° than those of the corresponding adducts of 1,2-difluoro-1,2-dichloroethylene (the corresponding isomers). The alcohols having the structure of $-CF_2\overset{|}{\underset{|}{C}}OH$ would be thought more acidic than those of $-\overset{|}{C}FCl\overset{|}{\underset{|}{C}}OH$. The difference of the boiling points between the two isomeric alcohols would be partly due to the difference of their acidity.

Oxidation of the secondary alcohols yielded the corresponding ketones which were identical with the 1:1 adducts of aldehydes to the corresponding halogeno olefins.[10] For example

$$CF_2{=}CCl_2 + C_3H_7OH \longrightarrow CHCl_2CF_2CH(C_2H_5)OH$$

$$\Big\downarrow \text{Oxidation}$$

$$CF_2{=}CCl_2 + C_2H_5CHO \longrightarrow CHCl_2CF_2COC_2H_5$$

Dehydration of the tertiary alcohols, such as $CHFClCFCl(CH_3)_2OH$, $CHCl_2CF_2C(CH_3)_2OH$, and $CHCl_2CFClC(CH_3)_2OH$, with phosphoric anhydride easily yielded the corresponding halogenobutene-1, $CHFClCFClC(CH_3){=}CH_2$, $CHCl_2CF_2C(CH_3){=}CH_2$, and $CHCl_2CFClC(CH_3){=}CH_2$, respectively. Although more difficult, dehydration of the secondary alcohols except $CHFClCFClCH(CH_3)OH$ also gave a small amount of corresponding unsaturated halogeno compounds. The physical properties of these new unsaturated halogeno compounds are listed in Table III.

Experimental[11]

Materials.—The chlorofluoro olefins used in the experiments were prepared by the dechlorination of the corresponding chlorofluoroethanes with zinc dust in ethanol or *n*-butyl alcohol according to the method of Henne, *et al.*[12] All of the alcohols used were purified by distillation.

Irradiation of γ-Ray. A mixture of the halogeno olefin and alcohol in a molar ratio of about 1:3 was added to a Pyrex tube 20 cm. × 5 cm. (*ca.* 300-ml. capacity). The reaction tube was then sealed and placed in the Co^{60} irradiation room for a period of 2 weeks to receive γ-irradiation at a rate of 0.8 × 10^5 r./hr. (total dosage *ca.* 2.7 to 2.9 × 10^7 r.).

Addition Reactions of Alcohols to 1-Fluoro-1,2,2-trichloroethylene.—A mixture of 83 g. (0.56 mole) of 1-fluoro-1,2,2-trichloroethylene and 82 g. (1.79 moles) of ethanol was sealed in a glass tube and irradiated at room temperature to a total dosage 2.9 × 10^7 r. for a period of 353 hr. Distillation of the irradiation products, after the removal of the unchanged olefin and alcohol, gave 72.5 g. (0.37 mole, 67% yield) of 3-fluoro-3,4,4-trichlorobutanol, b.p. 74–75° (10 mm.), and 4 g. of a residue. The infrared spectrum of the halogeno alcohol exhibited a free OH absorption band at 2.79 μ (shoulder) and a broad hydrogen bonded OH absorption band at 2.94 μ.

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[7] For the infrared spectrum of 1-chloro-2,2-difluoroethylene, J. R. Nielsen, C. Y. Liang, and D. C. Smith, *J. Chem. Phys.*, **20**, 1090 (1952).

[8] A. L. Henne and E. C. Ladd, *J. Am. Chem. Soc.*, **58**, 402 (1936).

[9] M. Hudlicky, "Chemie der organischen Fluorverbindungen," VEB Deutscher Verlag der Wissenschaften, Berlin, 1960, p. 219.

[10] H. Muramatsu and K. Inukai, *J. Org. Chem.*, **27**, 1572 (1962).

[11] All temperature readings are uncorrected.

[12] E. G. Locke, W. R. Brode, and A. L. Henne, *J. Am. Chem. Soc.*, **56**, 1726 (1934); ref. 8.

The addition reactions of methanol, *n*-propyl alcohol, and *i*-propyl alcohol to 1-fluoro-1,2,2-trichloroethylene were carried out under similar conditions.

Addition Reactions of Alcohols to 1,2-Dichloro-1,2-difluoroethylene.—In a glass tube were sealed 108 g. (0.81 mole) of 1,2-dichloro-1,2-difluoroethylene and 131 g. (2.84 moles) of ethanol. The contents of the tube were irradiated to a total dosage 2.8×10^7 r. for 327 hr. Distillation of the reaction mixture under reduced pressure yielded 58 g. (0.32 mole, 40% yield) of 3,4-dichloro-3,4-difluorobutanol-2, b.p. 66–69° (20 mm.), and 6 g. of a residue. The infrared spectrum of the halogeno alcohol exhibited a free OH absorption band at 2.77 μ (shoulder) and a broad hydrogen bonded OH band at 2.93 μ.

Using the same procedure, other alcohols were added to 1,2-dichloro-1,2-difluoroethylene.

Addition Reactions of Alcohols to 1,1-Dichloro-2,2-difluoroethylene.—A mixture of 103.5 g. (0.78 mole) of 1,1-dichloro-2,2-difluoroethylene and 107 g. (2.33 moles) of ethanol was irradiated to a total dosage 2.7×10^7 r. for 332 hr. Distillation of the irradiation products under reduced pressure gave 14.3 g. (0.08 mole, 10.2% yield) of 3,3-difluoro-4,4-dichlorobutanol-2, b.p. 74–76° (20 mm.), 2.3 g. (0.007 mole, 2% yield) of 3,3,5,5-tetrafluoro-4,4,6,6-tetrachlorohexanol-2, b.p. 95–98° (8 mm.), and 21 g. of a residue which seemed to be higher telomers. The infrared spectrum of the halogen alcohol, 1:1 adduct, showed a free OH adsorption band at 2.77 μ (shoulder) and a broad hydrogen bonded OH absorption band at 2.95 μ. The residue exhibited a sharp free OH band at 2.79 μ and a weak shoulder due to hydrogen bonded OH at about 2.90 μ.

Table I summarizes the yields and physical properties of the 1:1 adducts prepared by the addition of methanol, ethanol, *n*-propyl alcohol, and *i*-propyl alcohol to halogeno olefins. The yields and physical properties of the 1:2 adducts of alcohols to 1,1-dichloro-2,2-difluoroethylene are shown in Table II.

Oxidation of 2,3,3-Trichloro-2-fluoropropanol.—A mixture of 8 g. (0.04 mole) of 2,3,3-trichloro-2-fluoropropanol, 12 g. (0.04 mole) of potassium dichromate, 10 g. of concentrated sulfuric acid, and 30 ml. of water was stirred at about 85° for 3 hr. The mixture was filtered and the filtrate was extracted with diethyl ether. After the neutralization of the extracts with aqueous sodium hydroxide, 2.5 g. of water-insoluble product was separated. The product showed a carbonyl absorption band at 5.94 μ and seemed to be the ester of the reactant alcohol and acid formed by oxidation. From the aqueous layer 3 g. (0.014 mole) of sodium 1-fluoro-1,2,2-trichloropropionate was obtained.

Pyrolysis of Sodium 1-Fluoro-1,2,2-trichloropropionate.—Three grams (0.014 mole) of dried sodium 1-fluoro-1,2,2-trichloropropionate was heated at about 220° to yield 0.7 g. (0.005 mole) of an olefin in a trap cooled in Dry Ice–acetone. The infrared spectrum of the olefin was compared with 1,2-dichloro-1-fluoroethylene which was prepared by the dechlorination of 1,1,2,2-tetrachloro-1-fluoroethane.

Oxidation of 2,2-Difluoro-3,3-dichloropropanol.—A mixture of 9 g. (0.05 mole) of 2,2-difluoro-3,3-dichloropropanol, 17 g. (0.06 mole) of potassium dichromate, 10 g. of concentrated sulfuric acid, and 30 ml. of water was stirred at about 85° for 6 hr. The mixture was extracted with diethyl ether. Neutralization of the extracts with aqueous sodium hydroxide yielded 3.4 g. (0.02 mole) of sodium 1,1-difluoro-2,2-dichloropropionate.

Pyrolysis of Sodium 1,1-Difluoro-2,2-dichloropropionate.—Three grams (0.02 mole) of dried sodium 1,1-difluoro-2,2-dichloropropionate was heated at about 250° to give 1 g. (0.01 mole) of an olefin. The olefin was shown to be identical with the authentic sample[7] from its infrared spectrum.

Oxidation of 1,1-Dichloro-2,2-difluoropentanol-3.—Ten grams (0.05 mole) of 1,1-dichloro-2,2-difluoropentanol-3, 15 g. (0.05 mole) of potassium dichromate, 10 g. of concentrated sulfuric acid, and 50 ml. of water were stirred at 85° for 13 hr. The reaction mixture was extracted with diethyl ether, and 10 g. of water-insoluble product was isolated. Infrared spectral analysis showed that the product contained a strong C=O absorption band at 5.71 μ and was the mixture of the unchanged alcohol and ketone formed by oxidation. To 1.5 g. of the product in ethanol (10 ml.) was added a mixture of 0.5 g. of 2,4-dinitrophenylhydrazine, 2 ml. of concentrated sulfuric acid, 3 ml. of water, and 10 ml. of ethanol. In 10 min., a yellow-orange precipitate (0.7 g.) formed. Recrystallization of the crude 2,4-dinitrophenylhydrazone of the ketone from ethanol gave the orange crystals (0.3 g.). They did not show the depression of melting point when mixed with the hydrazone of the authentic sample, 1,1-dichloro-2,2-difluoropentanone-3.[10]

Dehydration of 2-Methyl-3,3-difluoro-4,4-dichlorobutanol-2.—A mixture of 18 g. (0.09 mole) of 2-methyl-3,3-difluoro-4,4-dichlorobutanol-2 and 18 g. (0.13 mole) of phosphoric anhydride was heated at about 150° for 30 min. and distilled. The distillate was washed with sodium bicarbonate solution and dried with anhydrous sodium sulfate. Fractionation of the product yielded 7 g. (0.04 mole) of 2-methyl-3,3-difluoro-4,4-dichlorobutene-1, b.p. 130–131°. Infrared spectral analysis showed that the product had a weak C=C absorption band at 6.01 μ but no OH band. The presence of the double bond was also indicated by the rapid absorption of bromine in the presence of sunlight.

Using the above procedure, 2-methyl-3,4-difluoro-3,4-dichlorobutene-1 and 2-methyl-3-fluoro-3,4,4-trichlorobutene-1 were obtained by dehydration of 2-methyl-3,4-difluoro-3,4-dichlorobutanol-2 and 2-methyl-3-fluoro-3,4,4-trichlorobutanol-2. They had the C=C absorption band at 6.04 μ and 6.05 μ, respectively.

Dehydration of 3,3-Difluoro-4,4-dichlorobutanol-2.—A mixture of 20 g. (0.11 mole) of 3,3-difluoro-4,4-dichlorobutanol-2 and 20 g. (0.14 mole) of phosphoric anhydride was heated at about 160° for 1 hr. and distilled to give 1.8 g. (0.01 mole) of 3,3-difluoro-4,4-dichlorobutene-1, b.p. 100–101°. The compound had a C=C infrared absorption band at 6.05 μ, but no OH band. The existence of the double bond was also indicated by bromination in the presence of sunlight.

Using the same procedure, 3-fluoro-3,4,4-trichlorobutanol-2 reacted with phosphoric anhydride to give a small amount of 3-fluoro-3,4,4-trichlorobutanol-2, but dehydration of 3,4-difluoro-3,4-dichlorobutanol-2 was not successful.

The physical properties and results of analyses of the halogenobutenes are shown in Table III.

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