the clear solution became turbid. After cooling, the residue was extracted with ethyl acetate and the extract evaporated to dryness. The yield was 0.07 g. (17%), m.p. 95–100°. The infrared spectrum showed strong bands at 5.75 μ (C = O), 6.45 μ (N—H deformation), and 6.87 μ (asymmetrical S—O stretch). A very weak band at 6.2 μ indicated the presence of a small amount of unreacted starting material.

Acknowledgment. The authors wish to express their thanks to C. A. Sperati of this laboratory for his guidance in this work and to R. D. Nelson for his assistance in the interpretation of the infrared data.

PARKERSBURG, W. VA.

[CONTRIBUTION No. 295 FROM THE RESEARCH DIVISION, ORGANIC CHEMICALS DEPARTMENT, E. I. DU PONT DE NEMOURS AND CO.]

ω-Hydroperfluoroalkylaldehydes by Photochlorination of α,α,ω-Trihydroperfluoroalkanols

NEAL O. BRACE

Received March 27, 1961

Photochlorination of α,α,ω-trihydroperfluoroalkanols at 10–40° gave good yields of ω-hydroperfluoroaldehydes which were recovered by distillation from the initially-formed hemiacetals. An 80% yield of 5-*H*-perfluoropentanal-1 at a 25% conversion of alcohol was obtained. The yield of ω-chloro-ω'-hydroperfluoroalkane and α,α-dihydrofluoroalkyl ester side-products was sensitive to reaction conditions. The fluorinated aldehydes are reactive intermediates for the preparation of stable hydrates, carbonyl derivatives, and decarbonylated products.

McBee, Pierce, and Marzluff[1] obtained perfluorobutyraldehyde by photochlorination of 1,1-dihydroperfluorobutanol in 24% conversion and 80% yield, but lithium aluminum hydride reduction of perfluoro acids or esters to the perfluoroaldehydes has been more frequently used,[2–4] since prior reduction of the acid to the alcohol is not required. An economical route to α,α,ω-trihydroperfluoroalkanols (I) is based on the telomerization of tetrafluoroethylene with methanol[5] and the family of alcohols thus made available can be conveniently oxidized directly to ω-*H*-perfluoroalkanals (II) by reaction with chlorine and light at low temperatures.[6] Success in this synthesis depends on the fact that the aldehydes remain combined as the much more stable hemiacetal of the parent alcohol during photochlorination; thermal cleavage occurs during subsequent distillation liberating the more volatile aldehyde. In this way the sensitive aldehyde is protected from destruction by light and chlorine and satisfactory yields of product are obtained. Additional data which relate to the preparation and some novel addition and replacement reactions of fluorinated aldehydes are reported in this paper.

Isolated yields of aldehyde (and side products) as a function of alcohol chain length, temperature, and amount of alcohol used up are listed in Table I. The conversion to 5-*H*-perfluoropentanal-1 increased with extent of reaction up to about 50% conversion of alcohol at 10–40°, with the best yield of about 80% obtained at 25% utilization of alcohol at 40°. Chlorination to 80% conversion of alcohol at 20° gave reduced *apparent* conversion and yield of aldehyde, and higher boiling condensation products. At 80°, a 75% conversion of alcohol gave 23% of 1-hydro-4-chloroperfluorobutane so that only 26% of aldehyde was recovered.

Photochlorination of 2,2,3,3-tetrafluoropropanol-1 occurred smoothly at 31°. Pyrolysis of the hemiacetal and isolation of the very reactive 2,2,3,3-tetrafluoropropanal-1 was facilitated by carrying the reaction to at least 40% conversion. At lower conversions, distillation of the unchanged alcohol together with the aldehyde occurred at a pyrolysis temperature high enough to crack the hemiacetal.

1,1,9-Trihydroperfluorononanol-1 and 1,1,11-trihydroperfluoroundecanol-1 melt at a temperature too high for satisfactory photochlorination. In the case of 1,1,11-trihydroperfluoroundecanol-1 in an inert solvent at 46°, hemiacetal formation evidently was so sluggish that 1-chloro-10-*H*-perfluorodecane (80% yield) was the main product. A liquid mixture of this alcohol and a large excess of 2,2,3,3-tetrafluoropropanol-1, however, gave none of the chlorohydroperfluoroalkanes, but a mixture of the two aldehyde hemiacetals.

A principal side product formed in these preparations was the α,α,ω-trihydroperfluoroalkyl ω-hy-

---

[1] E. T. McBee, O. R. Pierce, and W. F. Marzluff, *J. Am. Chem. Soc.*, **75**, 1609 (1953).

[2] D. R. Husted and A. H. Ahlbrecht, *J. Am. Chem. Soc.*, **74**, 5422 (1952).

[3] M. Braid, H. Iserson, and F. E. Lawlor, *J. Am. Chem. Soc.*, **76**, 4027 (1954).

[4] O. R. Pierce and T. G. Kane, *J. Am. Chem. Soc.*, **76**, 300 (1954).

[5] W. E. Hanford, U. S. Patent **2,559,628**, July 10, 1951.

[6] N. O. Brace, U. S. Patent **2,842,601**, July 8, 1958.

TABLE I

PHOTOCHLORINATION REACTIONS OF $H(CF_2CF_2)_nCH_2OH$

Reaction Conditions							Products					
$H(CF_2CF_2)_nCH_2OH$ (I)			Chlorine				$H(CF_2)_{2n}Cl$ (III)	$H(CF_2CF_2)_nCHO$ (II)		$H(CF_2CF_2)_nCOOH$	$H(CF_2)_{2n}COOCH_2(CF_2)_{2n}H$ (IV)	$H(CF_2)_{2n}COO\underset{OH}{\underset{\vert}{C}}H(CF_2)_{2n}H$ (V)
n	Moles	% Used Up	Moles Used	Time, Hr.	Temp.	HCl Moles	Yield,[a] % (g.)	Conv.,[b] %	Yield,[a] %	Yield,[a] % (g.)	Yield,[a] % (g.)	Yield,[a] % (g).
1	2.73	40	2.0	7	31	3.06	—	24	65	—	20	—
2[c]	3.00	[c]	5.9	5.0	110	7.6	55[d]	14.5	[c]	[c]	[c]	[c]
2	1.55	16	0.4	2.2	10	0.35	—	15	84	(4.9)	—	—
2	1.55	43	—	5.0	20	1.0	—	22	54	8	20	—
2	1.44	35	0.7	3.0	40	1.1	1.0	26	78	—	18	(7.0)
2	1.55	50	0.7	4.0	40	1.5	1.7	30	67	4.5	8.5	7.1
2	1.55	80	1.73	11.0	20	2.16	—	29[e]	23.5	—	(83)[f]	—
2	1.55	75	1.76	3.0	80	2.0	23	20	26	(5.0)	24	(7.0)
3	1.08	44	(0.66)	7.0	25	0.65	1.0	30	68	(2.2)	22.5	(7.0)
3	1.0	25	0.25	4.0	40	0.50	—	17	70	—	(6.8)	(1)
4	0.4[g]	63	—	1.0	55	0.46	14	29[h]	47	—	(24)[i]	—
5	0.18[j]	59	—	3.0	46	0.3	80[k]	—[l]	—	—	—	—

[a] Yields are calculated on basis of moles of product per moles of alcohol used up. [b] Conversion is calculated on basis of moles of product per moles of alcohol charged. [c] Reaction run in 1-l., round-bottom flask; alcohol not recovered from residue (167 g.). Internal coil ultraviolet source used. [d] Vapor phase chromatography analysis: 92% pure; 4.4% $H(CF_2)_4H$ and 3.3% $Cl(CF_2)_4Cl$ present. 13.6 g. of $Cl(CF_2)_4Cl$, b.p. 66° also isolated. [e] Contained 2% Cl or about 10% $H(CF_2)_4COCl$. [f] Ester cuts; b.p. 91° (16 mm.) to 93° (10 mm.); n_D^{25} 1.3257–1.3411; *Anal.* 5.5 and 12.7% Cl; infrared ester C=O at 5.57 μ. A series of higher b.p. cuts up to 120° (1.0 mm.); n_D^{25} 1.3420; 77.0 g.; (*Anal.* C, 26.0; F, 61.6; Cl, 6.2; mol. wt. 710) also obtained. Infrared no C=O band. [g] Dissolved in 175 cc. of carbon tetrachloride. [h] Aldehyde and aldehyde hydrate. [i] Two ester cuts, m.p. 89–91° and 46.5–65°; infrared on both showed no OH band at 3.00 μ; C=O at 5.55 μ. [j] Dissolved in 300 g. of perfluoropropylene "cyclic" dimer mixture. [k] B.p. 89° (30 mm.); m.p. 45.5–46.5°. [l] 1.2 g.; infrared C=O band at 5.65 μ; See Experimental for further details.

TABLE II

ω-HYDROPERFLUOROALKYLALDEHYDES AND DERIVATIVES

$H(CF_2CF_2)_nCHO$ (II)							Aldehyde Hydrates					2,4-Dinitrophenylhydrazones						
			Calcd.		Found[a]			Calcd.		Found			Calcd.			Found[a,b]		
	n_D^{25}	B.P.	C	F	C	F	M.P.	C	F	C	F	M.P.	C	F	N	C	F	N
n = 1	1.285	36.8	—	—	—	—	97–99[c]	24.3	51.4	24.7	54.0	127	34.8	24.4	18.0	34.7	24.3	18.0
2	1.295	86	26.1	66.0	26.1	65.9	50.5–51	24.2	61.3	24.3	60.7	97	32.2	37.0	13.6	32.0	36.8	13.7
3	1.298	125	25.4	69.1	25.6	70.2	74	24.1	65.6	24.7	65.4	80[d] (87–89)	30.6	44.7	10.9	30.6	45.0	11.1
4	1.3039	120 (200 mm.)	—	—	—	—	95–96	24.1	67.9	25.0	70.2	124.5	29.5	49.8	9.2	29.3	49.8	9.0
5	Solid	76–80[e] (10 mm.)	—	—	—	—	—	—	—	—	—	146	28.8	53.4	7.9	28.8	53.3	8.2

[a] F analysis by Wickbolt Method. [b] N analysis by Dumas Method. [c] Isolated as an azeotrope with water, also. See Experimental. [d] Two allotropic forms isolated; m.p. 80° and 87–89°, needles and stubby shafts. No depression on mixed m.p. Same analysis. [e] Not isolated in pure condition; 2,4-dinitrophenylhydrazone derivative prepared.

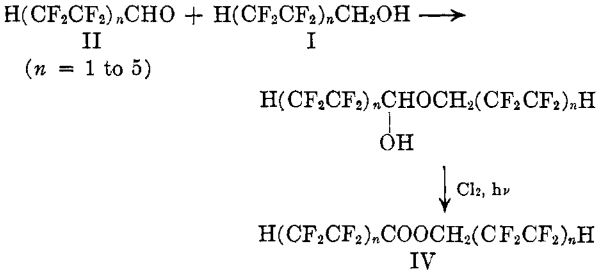
TABLE III

ESTERS OF ω-HYDROPERFLUOROALKANOIC ACIDS

	$H(CF_2)_{2n}COOCH_2(CF_2)_{2n}H$ (IV)						$H(CF_2)_{2n}COO\underset{OH}{\overset{H}{C}}—(CF_2)_{2n}H$ (V)					
			Calcd.		Found				Calcd.		Found	
n	B.P.	n_D^{25}	C	F	C	F	B.P.	n_D^{25}	C	F	C	F
1	91.5 (200 mm.)[a]	1.3173	27.7	58.5	—	58.2	—	—	—	—	—	—
2	47 (1.5 mm.)[a,c] 114 (40 mm.) 144 (200 mm.) 200 (760 mm.)	1.3146	26.1	—	26.1	—	182–186 (188 mm.)[b] 133–135 (20 mm.) 115 (12 mm.)	1.3200	25.2	63.8	25.2	63.6
3	138 (20.0 mm.)[a] 130 (16.0 mm.)	1.3153	25.5	69.1	25.3	71.1	169 (20 mm.)[b] 134 (1.0 mm.)	Solid	24.9	67.4	24.6	68.6
4	165 (15 mm.)[a] 158 (12 mm.) 151.5 (5.0 mm.)	M.p. 46.7–47°	25.2	70.6	24.1	71.4	—	—	—	—	—	—
5	102 (0.6 mm.)[a] 122 (3.0 mm.)	M.p. 50–51°	—	—	—	—	—	—	—	—	—	—

[a] Infrared spectrum Ester C═O at 5.55 μ only. [b] Infrared spectrum OH (strong) 2.95 μ; CH 3.37 μ; COOR 5.58 μ. [c] B.p. 93.4° (17 mm.).

droperfluoroalkanoate[7] (IV) apparently derived from the hemiacetal.

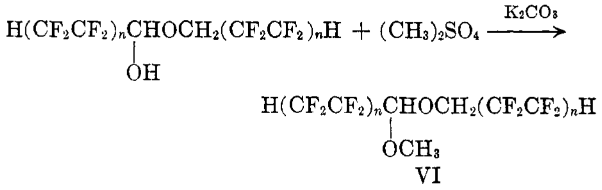


$$\underset{\text{II}}{H(CF_2CF_2)_nCHO} + \underset{\text{I}}{H(CF_2CF_2)_nCH_2OH} \longrightarrow H(CF_2CF_2)_n\underset{OH}{C}HOCH_2(CF_2CF_2)_nH \xrightarrow{Cl_2,\ h\nu} \underset{\text{IV}}{H(CF_2CF_2)_nCOOCH_2(CF_2CF_2)_nH}$$

(n = 1 to 5)

The ester IV was obtained in increasing amounts with higher conversions. At 43% utilization of 1,1,5-trihydroperfluoropentanol-1 a conversion of 11% to IV, 8% to free acid, and 22% to aldehyde (as hemiacetal) was obtained in five hours of reaction at 20°. At 16% conversion of this alcohol at 10° no ester was found. Some ω-hydroperfluoroalkanoic acid, and a half-ester of aldehyde hydrate, considered to be α,ω-dihydro-α-hydroxyperfluoroalkyl ω-hydroperfluoroalkanoate (V), were also isolated from these reaction mixtures. Traces of water reacted with the aldehydes to give the solid hydrates.

That the aldehydes were combined as hemiacetal during photochlorination of the alcohols was shown by: (1) The aldehyde 5.65 μ carbonyl absorption band in infrared spectra was entirely absent in samples removed during the course of reaction from mixtures containing as much as 30% of combined aldehyde. New infrared bands not present in the reactants were observed.[6] (2) Treatment of such a mixture with dimethyl sulfate and potassium carbonate[6] gave the stable, distillable ω-hydroperfluoroalkylaldehyde methyl α,α,ω-trihydroperfluoroalkyl acetal (VI). It was found that hemiacetal formation was catalyzed by acid, but bases were much more effective. VI was also isolated from the reaction of equimolar amounts of aldehyde, alcohol, potassium carbonate, and dimethyl sulfate.



$$H(CF_2CF_2)_n\underset{OH}{C}HOCH_2(CF_2CF_2)_nH + (CH_3)_2SO_4 \xrightarrow{K_2CO_3} \underset{\text{VI}}{H(CF_2CF_2)_n\underset{OCH_3}{C}HOCH_2(CF_2CF_2)_nH}$$

Reaction of any *free* aldehyde in the reaction mixture with chlorine could be completely avoided under synthesis conditions, but did occur at a temperature of above 40° or when the reaction mixture was diluted with a solvent. At 110° a 55% conversion of 1,1,5-trihydroperfluoropentanol-1 to 1-chloro-4-*H*-perfluorobutane and 14.5% to aldehyde was obtained. Free aldehyde alone in carbon tetrachloride gave a 64% yield in a rapid exothermic reaction.

$$H(CF_2CF_2)_2CHO + Cl_2 \xrightarrow[20\text{–}40]{h\nu} H(CF_2CF_2)_2Cl + CO + HCl$$

Unchanged aldehyde was recovered as a carbon tetrachloride azeotrope, and higher boiling condensation products were formed. There was no indication of acid chloride. At very low reaction temperatures it was possible to prepare ω-hydroperfluoropentanoyl chloride in 25% conversion by photochlorination of aldehyde.

$$H(CF_2CF_2)_2CHO + Cl_2 \xrightarrow[—20°]{h\nu} H(CF_2CF_2)_2COCl + HCl$$

The acid chloride distilled with the aldehyde and was identified by infrared spectrum (COCl band

---

(7) Esters of this class were first prepared by N. E. Wolff by heating I (n = 3) with excess bromine at 180°. See also D. R. Baer, *Ind. and Eng. Chem.*, **51**, 829 (1959).

at 5.55 μ). In view of the rapid conversion to chloroperfluoroalkane by chlorine and light at 20–40°, it does not seem likely that either aldehyde or acid chloride are present in the alcohol reaction mixtures to any significant extent, or that much ester is formed by acylation with acid chloride.

The aldehydes gave characteristic 2,4-dinitrophenylhydrazones. The melting points and analytical data are listed in Table II, together with the pertinent properties of the aldehydes and their hydrates. The esters which have been isolated from alcohol photochlorination product mixtures are listed in Table III.

A characteristic reaction[2] of fluorinated aldehydes is that of stable hydrate formation.

$$H(CF_2CF_2)_nCHO + H_2O \longrightarrow H(CF_2CF_2)_nCH(OH)_2$$

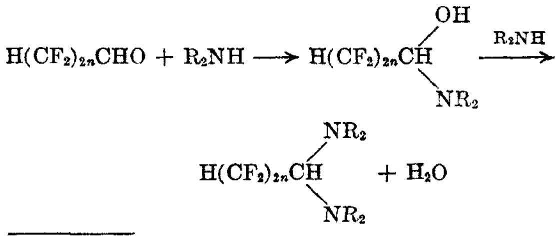
These products are crystalline, sublimable, very hygroscopic solids, and gave the aldehyde derivative on treatment with 2,4-dinitrophenylhydrazine. Dehydration of the hydrate to the free aldehyde, however, requires a strong dehydrating agent such as phosphorus pentoxide.[2–4] Storage of these aldehydes in 1,1,5-trihydroperfluoropentanol-1 is recommended since they may be recovered by simple distillation.

α,ω-Dihydroperfluoroalkanes were obtained in quantitative yield by treatment of aldehyde with concentrated aqueous alkali.[2]

$$\underset{\text{II}}{H(CF_2CF_2)_nCHO} + NaOH \longrightarrow H(CF_2CF_2)_nH$$
$$(n = 1,2,3)$$

1,2-Dihydroperfluoroethane has been reported,[8] but the boiling point given does not agree exactly with the boiling point we found. The identity of our product was ascertained by NMR spectra which showed only one peak ascribable to fluorine and one to hydrogen which is unique for this compound. The higher homologs also gave NMR spectra consistent with the α,ω-dihydroperfluoroalkane structure. The synthesis was conveniently carried out by adding the photochlorination product mixture containing II directly to the aqueous alkali.

Primary and secondary amines added readily exothermically to II. Addition of either one or two amine groups can occur to give either α-hydroxy-α,ω-dihydroperfluoroalkylamine or an α,α-diamino-α,ω-dihydroperfluoroalkane. Equimolar amounts of ethyleneimine and 7-*H*-perfluoroheptanal-1 gave 1-hydroxy-1-aziridinyl-1,7-dihydroperfluoroheptane in quantitative yield. The infrared spectrum in ether solution showed the free hydroxyl group at 3.00 μ, but in the solid phase the hydroxyl absorption band was shifted to 3.20 μ giving evidence for strong hydrogen-bonding. The monoadduct was also isolated in lower yield from reaction with two equivalents of amine. In this case, the liquid diamino product was produced as well.



$$H(CF_2)_{2n}CHO + R_2NH \longrightarrow H(CF_2)_{2n}CH(OH)(NR_2) \xrightarrow{R_2NH} H(CF_2)_{2n}CH(NR_2)_2 + H_2O$$

A primary amine, 1-amino-2-(2-hydroxyethylamino)ethane was allowed to react with an equimolar amount of 7-*H*-perfluoroheptanal-1, but the product which was distilled in 80% yield contained two amine residues. A corresponding amount of water and aldehyde were recovered. Intramolecular cyclization of the intermediate α-hydroxyamine having the β-NH group was anticipated, but apparently did not occur. Addition of the strongly basic primary amino rather than the hydroxyl group to the aldehyde carbonyl evidently was favored, since the product did not contain the primary amine function. Infrared analysis showed only a single OH and NH stretching band at 3.00 μ; the characteristic NH_2 bands were absent.

Reaction of ammonia with 5-*H*-perfluoropentanal-1 was briefly studied. Solid addition product was formed initially at 0° in ether solution; the oil which was isolated at room temperature was insoluble in water, was weaky basic, and contained only one amine residue.

EXPERIMENTAL

Photochlorination of α,α,ω-trihydroperfluoroalkanols. Photochlorination products and conditions are listed in Table I. The analyses of new compounds are listed in Tables II and III. The starting alcohols I used were the commercial materials dried by azeotropic distillation with benzene and redistilled. The reaction vessel, which contained a mercury vapor in quartz tubing internal ultraviolet source,[9] was purged with dry nitrogen. Plastic "Tygon" polyvinyl chloride tubing was used for connection to the cylinder of chlorine through an empty trap. The general procedure employed is illustrated with the photochlorination of I ($n = 2$); essential details are given for $n = 1$ and $n = 5$. I ($n = 2$) [360 g. (1.55 moles) b.p. 105° (200 mm.); n^{25}_D 1.3162] was placed in the irradiation vessel and cooled to a reaction temperature (inside) of 9 to 11°, with the bath at 0°. Chlorine gas was fed in over a 2.4-hr. period at a 12 g./hr. rate, with no visible excess in the reaction. The hydrogen chloride which was evolved was conducted through a trap immersed in a −80° cooled bath and absorbed in water. The acid solution was titrated with standard alkali; a total of 0.35 equivalent of acid was absorbed. The cold trap contained a small amount of condensed yellow liquid identified as chlorine. The reactor liquid (357.5 g.) was transferred to a 3-ft. platinum spinning band (Column A) distillation apparatus and fractionated. There was obtained 47.0 g. (a 15% conversion or 84% yield on I used up) of II ($n = 2$), b.p. 83–86°, n^{25}_D 1.295–1.300, which distilled slowly when the pot temperature reached 140°. The main fraction had a b.p. of 85.5°; n^{25}_D 1.295. Its infrared absorption spectrum showed a CH band at 3.45 (CF_2H) and at 3.52 μ, and the strong aldehyde carbonyl band at 5.65 μ. A trace of II

---

(8) A. L. Henne and M. W. Renoll, *J. Am. Chem. Soc.*, **58**, 887 (1936).

(9) M. S. Kharasch and H. N. Friedlander, *J. Org. Chem.*, **14**, 239 (1949).

hydrate, probably formed in loading the infrared cell, gave a very weak band at 2.85 μ. The solid hydrate formed immediately on exposure of the dry liquid II to moist air. A *2,4-dinitrophenylhydrazone* derivative, m.p. 95.5–96.5°, was prepared in quantitative yield in $6N$ sulfuric acid solution of 2,4-dinitrophenylhydrazine.

II ($n = 5$) *and II* ($n = 1$) *from a mixture of I* ($n = 1$ *and* 5). A mixture of I ($n = 1$, 262 g.; 2.0 moles) and I ($n = 5$, 89.0 g.; 0.167 mole) (a 12 to 1 mole ratio) gave a liquid mixture at 39°. At this temperature, 0.5 equivalent of acid was evolved during 5 hr. of chlorination using 0.58 mole of chlorine. Distillation gave II ($n = 1$), 45 g. (19% conversion, 67% yield) b.p. 36–36.8°; n_D^{25} 1.285 recovered from the trap liquid; II ($n = 5$), 9.0 g. (10% conversion, 38% yield), b.p. 76–80° (10 mm.) distilled after excess I ($n = 1$) was removed.

Preparation of aldehyde, ester IV and acetal VI from I. ($n = 1$). I ($n = 1$; 360 g.; 2.73 moles; b.p. 107°; n_D^{25} 1.3192) at 31° (bath at 18–20°) during a 7-hr. period at a 20 g./hr. chlorine feed rate used up 137 g. (2.0 moles) of chlorine, and gave 3.06 moles of acid vapors. The colorless solution weighed 355 g.; n_D^{25} 1.3300; and had an infrared spectrum which showed strong ester carbonyl at 5.55–5.60 μ, but no free aldehyde. Distillation of a 60.0 - g. aliquot in Column A at 200 mm. pressure gave 33.0 g. of recovered I ($n = 1$), b.p. 70–74°; n_D^{25} 1.3259 to 1.3228 (60% recovery) and 9.5 g. of IV ($n = 1$), n_D^{25} 1.3173; b.p. 91.5° (20% yield). The −80° trap contained 14.3 g. of II ($n = 1$), b.p. 36.8°; n_D^{25} 1.285 (24% conversion or 65% yield based on recovered I). The aldehyde was extremely reactive to atmospheric moisture, had an intense odor, and was too unstable at 25° for keeping. Reaction of 200 g. of the reaction product mixture with 126 g. (1.0 mole) of methyl sulfate and 135 g. (1.0 mole) of potassium carbonate gave 89.0 g. (70%) of VI (n = 1), b.p. 157–160°; n_D^{25} 1.3294.

Anal. Calcd. for $C_7F_8H_8O_2$: C, 30.4; F, 55.0. Found: C, 30.2; F, 54.6.

Photochlorination of II ($n = 2$) *to III* ($n = 2$) *or to 5-hydroperfluoropentanoyl chloride.* A solution of 50 g. (0.22 mole) of II ($n = 2$) in 159 g. of carbon tetrachloride was irradiated at 22°. As chlorine was bubbled in, the temperature rose to 32° in 10 min. and further to 40° in 25 min. At this point ice was added to the bath to reduce the temperature to 22° again. After 1 hr., 5 g. of chlorine (0.14 g.-atom) had been used, and an excess of chlorine appeared. The acid gases evolved required 0.15 equivalent of base for neutralization. Distillation of the liquids in the reactor and −80° cold trap gave 27.6 g. (0.12 mole) of III ($n = 2$) (54% conversion of II), b.p. 50° and about 5 g. (10%) of recovered II (as carbon tetrachloride azeotrope), b.p. 68–72°; n_D^{25} 1.3758 (50% II).

The material with boiling point above carbon tetrachloride (12.5 g.) was partly solid of an indefinite melting point having an infrared spectrum which showed no OH of the aldehyde hydrate but prominent CF bands at 8.50, 8.85, and 9.80 μ and C—Cl absorption at 12.80 μ. The liquid portion was not distillable at 60° (12 mm.).

II ($n = 2$) (82.3 g.; 0.36 mole) was allowed to react with chlorine at −20° to −10°. Distillation using a high reflux ratio in Column A gave 2.6 g. of III ($n = 2$), b.p. 49–50°; n_D^{25} 1.292 (a 6.6% conversion); 3.9 g. of an intermediate fraction containing a small amount of III and mostly II (6.3% chlorine) and 67 g. of a constant boiling mixture of 5-hydroperfluoropentanoyl chloride and II, b.p. 85°. The pure acid chloride has a b.p. of 87–88°. Analysis (3.2% Cl) showed these fractions contained 23% acid chloride or 25% conversion. Infrared absorption spectra showed two bands in the carbonyl region, a moderate band at 5.55 μ (COCl) and a strong band at 5.65 μ.

Conversion of II to II hydrates; II ($n = 1$) *hydrate.* II ($n = 1$) (20.0 g., 0.154 mole) in a 500-cc., round-bottom flask fitted with a Dry Ice–cooled reflux condenser, a nitrogen inlet and stirrer was stirred while 2.78 cc. (0.154 mole) of water was added from a calibrated syringe through a rubber plug. Refluxing occurred and the liquid product crystallized to a mushy solid; m.p. (sinter 96.4°) 97.8–98.6° dec., dried on a clay plate. The solid when exposed to moist air quickly melted down. A benzene and ether wash left 2.1 g., m.p. (sinter 93.4°) 94.8–96.5° dec.

An infrared spectrum of the liquid product above showed a strong, broad hydroxyl band at 2.80–3.10 μ; no CH or C═O stretching bands, and two strong bands at 11.95 and 12.90 μ. The solid m.p. 98°, in a melt smear had OH bands at 2.80 and 2.95 μ and no C═O band, whereas a Nujol mull of the solid gave only a single OH band at 3.00 μ. The benzene-ether filtrate above (12.0 g.) was fractionated in a 16 in. tantalum spinning band column. A forerun fraction, b.p. 98–104°; n_D^{25} 1.3508; 1.07 g. was removed; the remainder all distilled at 104°; n_D^{25} 1.3459 and 1.3504 in two cuts; 10.2 g., leaving 0.3 g. of hold-up. These fractions remained as liquids and were found by analysis to be an azeotrope of II ($n = 1$) hydrate with 17% water.

Distillation of 10 cc. of benzene from 2.0 g. of the liquid product gave a water-benzene-II ($n = 1$) azeotrope, b.p. 72–76°, leaving 0.36 g. of oil residue which did not solidify. Reaction of the benzene solution with 1.6 g. of 2,4-dinitrophenylhydrazine in warm $6N$ sulfuric acid solution gave a deposit of yellow 2,4-dinitrophenylhydrazone of II ($n = 1$), 2.0 g., m.p. 124.6–125°.

II ($n = 2$) *hydrate.* The solid recrystallized from warm benzene, was kept in a nitrogen-filled box and a capillary loaded; m.p. 50.5–51.0°. An infrared spectrum of the solid had a very strong OH band at 3.08 μ; no C═O; CH at 7.14 μ, CF at 7.75–10.0 μ, and prominent bands at 11.10, 11.55. 12.15, and 12.95 μ. A second crop of crystals, m.p. (sinter 44.5°) 46.5–48.0°, was dried in the nitrogen box, loaded into a sublimation tube and sublimed under an argon atmosphere at an oil bath temperature of 108°; m.p. 49–51.3°. II ($n = 2$) hydrate distilled as a constant boiling mixture with water, b.p. 104–105°, n_D^{25} 1.3338 containing 27.5% water.

II ($n = 3$) *hydrate.* This compound was not noticeably hydroscopic. An infrared spectrum (melt smear) showed a broad strong OH band at 2.95–3.10 and no C═O band, while a Nujol mull had a sharp OH band at 3.03 μ, but a shoulder at 2.95 μ was also apparent. Besides CF bands, characteristic bands at 10.83, 12.10, 12.55, 13.30, and 14.10 μ appeared. There was no band at 10.40 μ (963 cm.$^{-1}$) cited[2] for perfluorobutyraldehyde hydrate in any of these products.

Reaction of II ($n = 2$) *with ammonia.* Ammonia was bubbled for 2 hr. into a solution of 20.0 g. (0.087 mole) of II ($n = 2$) in 100 cc. of anhydrous ether at 0° under a nitrogen atmosphere. The clear solution became slightly cloudy as a white solid formed. Ether was allowed to evaporate while nitrogen was bubbled in overnight. A colorless oil remained. Its infrared spectrum showed NH and OH bands at 3.00 to 3.20 μ, CH at 3.39 and 3.50 μ (contained some ether, see below); no C═O at 5.65 μ or at 6.00 μ. The product was the aldehyde-ammonia addition compound having a very weakly basic amino group.

Anal. Calcd. for $C_5F_8H_5ON$: C, 24.3; F, 61.5; N, 5.56. Found: C, 29.4; F, 60.5; N, 3.5.

Some ether remained in the sample as indicated by high C and low F and N.

The product was insoluble in water, but addition of a few drops of concentrated hydrochloric acid to a few drops of product gave a white soft solid precipitate which gave a clear solution with heat evolution upon the addition of 5 cc. of water. When the solution was made alkaline with concentrated ammonium hydroxide, the oil separated again and was extracted into ether.

Reaction of II ($n = 3$) *with ethyleneimine. At a 1:1 mole ratio.* A solution of 2.15 g. (0.05 mole) of ethyleneimine in 50 cc. of anhydrous ether was chilled to 0° and stirred under nitrogen while 15 g. (0.05 mole) of II ($n = 3$) was added dropwise at 4–6° over a 40-min. period, followed by 10 cc. of ether. A 5-ml. aliquot was diluted to 25 ml. with ether and an infrared spectrum versus ether had a single

OH(NH) band at 3.00 μ, a weak CH band at 3.25 μ; *no* aldehyde C═O band at 5.65 μ and *no* ethyleneimine bands at 10.95, 11.70, or 12.80 μ. There were present new bands at 8.30, 11.50, 12.00, 12.70, 13.10, 13.85, and 14.30 μ. An infrared spectrum of the solid product (m.p. 67–68°, recrystallized from benzene) which was isolated by evaporating ether from a portion of the solution was quite different. A melt smear showed no OH or NH band at 3.00 μ, but a strong band at 3.20 μ; CH deformation bands at 6.70–8.00 μ, CF bands at 8.25–10.00 μ, and new bands 10.65, 11.30, 11.65, and 14.50 μ. Bands at 10.80, 11.50, 13.10, 13.85, and 14.30 μ had disappeared. However, an ether solution freshly prepared from the isolated solid compound was identical to the original ether solution. *1-Hydroxy-1-aziridinyl-1,7-dihydroperfluorohexane* (VII) was analyzed.

Anal. Calcd. for $C_9H_{12}H_7NO$: C, 28.99; F, 61.1; N, 3.76. Found: C, 28.4; F, 61.9; N, 3.9.

At a 2:1 mole ratio. A solution of 7.94 g. (0.185 mole) of ethyleneimine in 100 cc. of dry ether was stirred at 0° while 30.0 g. (0.091 mole) of II ($n = 3$) was added during 45 min. The reaction temperature rose to 7–8° during the addition. Ether and unchanged ethyleneimine were evaporated under nitrogen, leaving 45.3 g. of liquid. A solid, m.p. 63–64°, 0.74 g., separated on cooling which gave an analysis corresponding to VII. Complete removal of ether from the product left 37.5 g. of liquid (100% yield for 2:1 addition product), but on standing, more crystals of VII began to form and distillation of 10.0 g. of the product mixture gave 3.9 g. of VII as a white solid which sublimed at 83–78° (0.7 mm.); m.p. 61–66°. Analysis and infrared spectra showed its identity with VII, m.p. 67–68°, isolated above. The 2:1 addition compound decomposed during distillation to a dark brown tar.

Reaction of II ($n = 3$) with 1-amino-2-(2-hydroxyethylamino)ethane. A solution of 33.0 g. (0.10 mole) of II ($n = 3$) in 50 cc. of dry benzene was stirred while 10.4 g. (0.10 mole) of 1-amino-2-(2-hydroxyethylamino)ethane was added over a 0.5-hr. period. The temperature rose from 23 to 60.5° in 10 min. and fell to 40° during the addition. The solution was distilled in Column A. Benzene, a water layer (2.0 cc.) and unchanged II ($n = 3$) (52.3 g.) distilled at 45–52° (300 mm.). The product taken in three fractions, b.p. 96° (1.0 mm.); n_D^{25} 1.3958–1.3998; 28 g., was obtained in 80% yield. (The residue was 1.7 g.) *N,N″-(7-H-dodecafluoroheptylidene)bis-[N′-(2-hydroxyethyl)ethylenediamine]* (VIII) was a viscous, colorless oil which was insoluble in water and 0.1*N* hydrochloric acid, but soluble in 1.2*N* hydrochloric acid. VIII reduced the surface tension of aqueous hydrochloric acid solution to 35.6 dynes/cm. at 2.0% concentration. An infrared spectrum showed a weak OH(NH) band at 3.00 μ, strong CH bands at 3.40 and 3.45 μ, and a large number of bands above 7.00 μ. The properties and analysis of VIII are consistent with the structure $H(CF_2)_6CH(NHCH_2CH_2NHCH_2CH_2OH)_2$.

Anal. Calcd. for $C_{15}F_{12}H_{24}N_4O_2$: C, 34.6; F, 43.8; H, 4.65; N, 10.75. Found: C, 36.6; F, 45.0; H, 3.7; N 10.2.

1,2-Dihydroperfluoroethane.[9,10] I ($n = 1$) (1030 g., 7.8 moles) was treated with chlorine (180 g., 2.54 moles) as above over a 6-hr. period. Hydrogen chloride was removed by sweeping with nitrogen and the crude mixture added dropwise to 50% aqueous potassium hydroxide solution. The gases evolved were collected in a trap, cooled in solid carbon dioxide, and redistilled, b.p. −19°; 164 g. (20% conversion, 63% yield based on chlorine); reported[8] b.p. −23°. NMR spectra showed only one peak ascribable to fluorine and one to hydrogen. Such a simple spectrum could only be given by the symmetrical molecule 1,2-dihydroperfluoroethane.

1,4-Dihydroperfluorobutane.[10] II ($n = 2$) (15 g., 0.065 mole) was dropped into 30 cc. of 50% aqueous potassium hydroxide solution. Heat developed and a gas was given off which was condensed and redistilled, b.p. 45°. NMR spectra indicated the presence of CHF_2 and CF_2 groups in the molecule.

1,6-Dihydroperfluorohexane.[10] II ($n = 3$) (25.0 g., 0.096 mole) was dropped into 100 cc. of 50% aqueous potassium hydroxide solution and refluxed for 1 hr. The organic layer after cooling was separated, washed alkali-free with water, dried, and distilled to give 22.9 g. (100%) of 1,6-dihydroperfluorohexane, b.p. 92.5°.

Anal. Calcd. for $C_6F_{12}H_2$: C, 23.8; F, 75.5. Found: C, 24.9; F, 75.9.

An NMR spectrum was consistent with the structure assigned.

WILMINGTON, DEL.

---

[10] I am indebted to J. F. Smith for this experiment.

[CONTRIBUTION NO. 674 FROM THE CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND CO.]

Iminosulfur Oxydifluorides

RICHARD CRAMER AND D. D. COFFMAN

Received April 11, 1961

A new class of sulfur compounds, the iminosulfur oxydifluorides, $R—N═SOF_2$, has been obtained by the reaction of primary amines with sulfur oxytetrafluoride.[1] Iminosulfur oxydifluorides are moderately resistant to hydrolysis, resembling, in this respect, sulfuryl fluoride, but react readily with the more basic amines. When attached to a benzene ring, the iminosulfur oxydifluoride group directs electrophilic substituents to the *para* position and is mildly activating.

Sulfuryl fluoride, SO_2F_2, reacts with ammonia[2] to give sulfamide (Equation 1), while thionyl fluoride, SOF_2, with ammonia and primary amines yields imines (Equations 2 and 3).[3]

$$NH_3 + SO_2F_2 \longrightarrow NH_2SO_2NH_2 \tag{1}$$

$$RNH_2 + SOF_2 \longrightarrow RNHSOF \tag{2}$$

$$RNHSOF \longrightarrow RN{=}SO \tag{3}$$

When sulfur oxytetrafluoride, SOF_4, became easily accessible,[4,5] a study of its reaction with

---

[1] As this paper was in preparation for publication, F. Seel and G. Simon published a note [*Angew. Chem.*, **72**, 709 (1960)] which mentions the reaction of amines with sulfur oxytetrafluoride to give, apparently, iminosulfur oxydifluorides. No specific compounds are mentioned.

[2] W. Traube and E. Reubke, *Ber.*, **56**, 1661 (1923).

[3] M. Goehring and G. Voigt, *Ber.*, **89**, 1050 (1956).

[4] C. W. Tullock, F. S. Fawcett, W. C. Smith, and D. D. Coffman, *J. Am. Chem. Soc.*, **82**, 539 (1960).