TABLE VI

PRODUCTS FROM IRRADIATION OF *n*-HEPTAFLUOROBUTYRYL BROMIDE AND HEXAFLUOROPROPYLENE

Compd.	B.p., °C.	Formula	Carbon, %		Bromine, %		Fluorine, %	
			Calcd.	Found	Calcd.	Found	Calcd.	Found
XVII	154–155	C_9BrF_{19}	19.7	19.4	14.6	14.9	65.7	65.4
XVIII	132–145	$C_6Br_2F_{12}$	15.7	15.4	34.7	34.0	49.6	48.5
XVI	90–100	C_6BrF_{13}			20.0	20.9	61.9	61.6

bleeding of the vessel through a small Dry Ice cooled trap there collected less than 0.5 ml. of condensate. The residue was examined by gas chromatography and shown to be almost entirely perfluorobutyryl chloride. The chromatogram indicated the presence of just traces of *n*-perfluorohexane and 1-chloroheptafluoropropane.

F. **Preparation of Starting Materials.** 1. **5-H-Octafluorovaleryl Bromide.**[18]—Benzoyl bromide (120 g., 0.648 mole) was placed in a flask fitted with a paddle stirrer, thermometer, addition funnel, and short-path still head. The still head was connected to an ice-cooled receiver and then to a Dry Ice cooled trap. 5-H-Octafluorovaleric acid[19] (100 g., 0.406 mole) was added during 0.5 hr. The mixture was heated to 150° and then the system was evacuated with a water pump until no more material collected in the receiver. The contents of the trap and receiver were combined and distilled through a small spinning-band still. There was thus obtained 42.43 g. (34%) of 5-H-octafluorovaleryl bromide distilling at 100–103° (mostly 103°).

Anal. Calcd. for C_5HBrF_8O: C, 19.4; H, 0.3; Br, 25.9; F, 49.2. Found: C, 19.9; H, 0.8; Br, 26.0; F, 49.3.

2.—**Perfluorobutyryl bromide** was prepared in the manner described in 1 from 186 g. (1.0 mole) of benzoyl bromide and 140 g. (0.64 mole) of perfluorobutyric acid (Columbia Organic Chemicals Co.). There was obtained 74.3 g. (41%) of perfluorobutyryl bromide distilling at 55–57°; lit.[20] b.p. 52–54° (748 mm.).

3.—**Perfluorobutyryl chloride** was obtained from Columbia Organic Chemicals Co., and **perfluoroglutaryl chloride** was obtained from Hooker Electrochemical Co., Inc. Each was redistilled before use.

4. **Perfluorooctanoyl Chloride.**—A mixture of 200 g. (0.494 mole) of perfluorooctanoic acid (Columbia Organic Chemicals Co.) and 200 g. (1.02 moles) of α,α,α-trichlorotoluene was refluxed for 5 hr. Upon distillation of the reaction mixture through a spinning-band still, there was obtained 179.4 g. (86%) of perfluorooctanoyl chloride distilling at 134–135°, $n^{25}\mathrm{D}$ 1.3080; lit.[21] b.p. 129–130°, $n^{25}\mathrm{D}$ 1.3025.

5.—**5-H-Octafluorovaleryl chloride** was prepared in the manner described in 4 from 300 g. (1.53 mmoles) of α,α,α-trichlorotoluene and 200 g. (0.81 mole) of 5-H-octafluorovaleric acid. Upon distillation there was obtained 185.5 g. (86%) of 5-H-octafluorovaleryl chloride distilling at 83–85°; lit.[22] b.p. 84.6–86.6°.

6. **Perfluorooctanoyl Fluoride.**[23]—A mixture of 164 g. (0.396 mole) of perfluoroooctanoic acid and 50 g. (0.46 mole) of sulfur tetrafluoride was heated in a stainless steel autoclave at 60° for 9 hr. The reaction mixture was placed in a plastic container, and diluted with 150 ml. of pentane; then 20 g. (0.48 mole) of dry powdered sodium fluoride was added. The mixture was stirred for 0.25 hr., filtered, and distilled through a spinning-band still. There was obtained 87.4 g. (53%) of perfluorooctanoyl fluoride distilling at 108°.

Anal. Calcd. for $C_8F_{16}O$: C, 23.1; F, 73.1. Found: C, 23.6; F, 72.9.

7. **5-H-Octafluorovaleryl Fluoride.**—A mixture of 100 g. (0.378 mole) of 5-H-octafluorovaleryl chloride, 30 g. (0.714 mole) of powdered sodium fluoride, and 100 ml. of tetramethylene sulfone was heated in an autoclave at 100° for 2 hr. and then at 125° for 4 hr. Upon distillation of the reaction mixture through a spinning-band still, there was obtained 42.9 g. (46%) of 5-H-octafluorovaleryl fluoride distilling at 60–61°.

Anal. Calcd. for C_5HF_9O: C, 24.2; H, 0.4; F, 68.9. Found: C, 24.6; H, 0.6; F, 67.0.

8.—**Perfluorobutyryl fluoride** was prepared from perfluorobutyric acid and carbonyl fluoride as described by Fawcett, Tullock, and Coffman.[24]

9.—**Perfluoroglutaryl fluoride** was prepared in the manner described in 6 above from 100 g. (0.416 mole) of perfluoroglutaric acid (Columbia Organic Chemicals Co.) and 115 g. (1.07 moles) of sulfur tetrafluoride (9 hr. at 75°). After work-up there was obtained 40.2 g. (40%) of perfluoroglutaryl fluoride distilling at 46–47°.[25]

10.—**ω-Chloroperfluorononanoyl fluoride** was prepared as described previously.[26]

---

[18] This procedure was adapted from that described by J. M. Tinker [U. S. Patent 2,257,868 (1941); *Chem. Abstr.*, **36**, 495 (1942)].

[19] This acid was prepared by permanganate oxidation of the corresponding alcohol according to the procedure described by K. L. Berry [U. S. Patent 2,559,629 (1951); *Chem. Abstr.*, **46**, 3063 (1952)].

[20] A. M. Lovelace, D. A. Rausch, and W. Postelnek, "Aliphatic Fluorine Compounds," Reinhold Publishing Corp., New York, N. Y., 1958, p. 225.

[21] M. Hauptschein, J. F. O'Brien, C. S. Stokes, and R. Filler, *J. Am. Chem. Soc.*, **75**, 87 (1953).

[22] J. E. Carnahan and H. J. Sampson, U. S. Patent 2,646,449 (1953); *Chem. Abstr.*, **48**, 7048 (1954).

[23] This procedure is similar to that described by W. R. Hasek, W. C. Smith, and V. A. Engelhardt [*J. Am. Chem. Soc.*, **82**, 543 (1960)].

[24] F. S. Fawcett, C. W. Tullock, and D. D. Coffman, *ibid.*, **84**, 4275 (1962).

[25] Previously reported: b.p. 41–47° [R. D. Smith, F. S. Fawcett, and D. D. Coffman, *ibid.*, **84**, 4285 (1962)]; b.p. 47–48° [R. F. Sweeney and C. Woolf, U. S. Patent 3,018,306 (1962); *Chem. Abstr.*, **56**, 15363 (1962)].

[26] N. O. Brace and W. B. McCormack, *J. Org. Chem.*, **26**, 5098 (1961).

Hydrogen Sulfide Adducts of Chloral, Fluoroaldehydes, and Fluoro Ketones[1]

J. F. HARRIS, JR.

Contribution No. 1055 from the Central Research Department, Experimental Station,
E. I. du Pont de Nemours and Company, Wilmington 98, Delaware

Received February 10, 1965

Under pressure, hydrogen sulfide reacts with chloral and fluorinated aldehydes and ketones to form 1:1 adducts. The stabilities and some chemical properties of these adducts were investigated.

The reactions of hydrogen sulfide with carbonyl compounds have yielded a variety of products including *gem*-dithiols, trithianes, thiocarbonyl compounds, unsaturated sulfides, enethiols, saturated thiols, hydroxy sulfides, and polysulfides.[2] The nature of the product (or products) obtained depends largely upon the structure of the carbonyl substrate and the reaction conditions employed. It seems logical that the initial molecular product formed in many, if not all, of these reactions is the simple addition product, an olthiol (I),

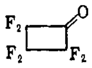
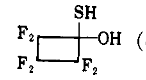
---

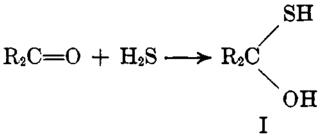
[1] A communication of this work has appeared: J. F. Harris, Jr., *J. Org. Chem.*, **25**, 2259 (1960).

[2] E. Campaigne, in "Organic Sulfur Compounds," N. Kharasch, Ed., Pergamon Press Inc., New York, N. Y., 1961, p. 134.

TABLE I

PREPARATION OF HYDROGEN SULFIDE ADDUCTS

Starting material (g., mole)	Moles of H_2S/mole of carbonyl compound	Conditions	Product (%)
Cl_3CCHO (11, 0.0745)	8.68	Autogenous pressure, room temp., 15 hr.	$Cl_3CCH(OH)SH$ (22)
CF_3CHO (18, 0.183)	4.02	Autogenous pressure, room temp., 18 hr.	$CF_3CH(OH)SH$ (57)
C_2F_5CHO (31, 0.209)	3.4	Autogenous pressure, room temp., 16 hr.	$C_2F_5CH(OH)SH$ (66)
n-C_3F_7CHO (16, 0.081)	14.6	Autogenous pressure, room temp., 18 hr.	n-$C_3F_7CH(OH)SH$ (70)
$H(CF_2)_4CHO$ (23.5, 0.102)	8.6	Autogenous pressure, room temp., 18 hr.	$H(CF_2)_4CH(OH)SH$ (72)
CF_3COCF_3 (12.0, 0.0723)	6.3	Autogenous pressure, room temp., 2.5 days	$(CF_3)_2C(OH)SH$ (84)
$ClCF_2COCF_2Cl$ (50, 0.251)	5.8	Autogenous pressure, 80°, 5 hr.	$(ClCF_2)_2C(OH)SH$ (81)
$ClCF_2COCFCl_2$ (20, 0.0929)	5.7	Autogenous pressure, room temp., 2.5 days	$ClCF_2(Cl_2CF)C(OH)SH$ (69)
$C_2F_5COC_2F_5$ (32, 0.120)	7.3	Autogenous pressure, 80°, 5 hr.	$(C_2F_5)_2C(OH)SH$ (32.5)
n-$C_3F_7COC_3F_7$-n (32, 0.088)	20	2000 atm., 80°, 5 hr.	$(n$-$C_3F_7)_2C(OH)SH$ (28)
 (27, 0.152)	7.7	Autogenous pressure, room temp., 2.5 days	 (82)



$$\mathrm{R_2C{=}O + H_2S \longrightarrow R_2C}\begin{matrix}\diagup\ \mathrm{SH}\\ \diagdown\ \mathrm{OH}\end{matrix} \qquad (1)$$

I

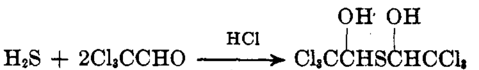
and that the materials actually isolated result from further reactions of this intermediate. This idea was put forward 75 years ago by Baumann(3) to help explain the products obtained from the reaction of formaldehyde and acetaldehyde with H_2S. Although some oxygen-containing thiol compounds were characterized, apparently 1:1 adducts were not isolated.(4) 1,1-Olthiols have been proposed as intermediates in the reduction of aldehydesulfoxylic acids,(5) but none apparently was actually isolated.

In more recent times, the intermediacy of 1,1-olthiols in reactions of hydrogen sulfide with carbonyl compounds has continued to be proposed,(2,6–8) but no isolation of such an intermediate has been reported.

This paper presents the results of a study which has been made of the reactions of chloral and fluorinated aldehydes and ketones with H_2S leading to 1:1 adducts. The results of the experiments are tabulated in Tables I and II.

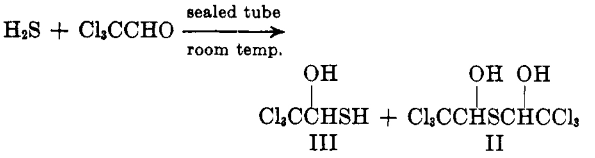
Results and Discussion

Aldehydes.—Previous studies of the reactions of hydrogen sulfide with halogenated aldehydes under mild conditions have been limited to chloral. These reactions, carried out in organic or aqueous solvents, usually in the presence of hydrogen chloride, have yielded the 2:1 chloral–H_2S adduct II (eq. 2). It has now been found that, if chloral is sealed in a pressure vessel with an appreciable excess of hydrogen sulfide and allowed to stand at room temperature for several hours, the major product is the 1:1 adduct, 1-hydroxy-2,2,2-trichloroethanethiol (III). There is also obtained some of the 2:1 adduct II (eq. 3a), and it was shown in a separate experiment that III reacts readily with chloral to give II (eq. 3b). The 1:1 adduct exhibits characteristic OH and SH infrared bands and can be distilled at reduced pressure. However, shortly after distillation, on standing at room temperature, III becomes cloudy, precipitates solid, concurrently evolves H_2S, and, after a few days, has been quantitatively converted to II, no doubt *via* the two-step sequence shown in eq. 4. It thus seems likely that the II obtained in the reaction represented by eq. 3a arose from III and that, in those previously described experiments involving H_2S and chloral or chloral hydrate, from which only II was isolated, III was indeed an intermediate.



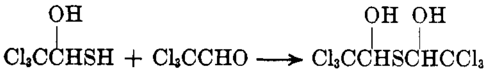
$$\mathrm{H_2S + 2Cl_3CCHO \xrightarrow[\text{ether, water, etc.}]{HCl} Cl_3C\overset{OH}{C}HS\overset{OH}{C}HCCl_3} \qquad (2)$$

II

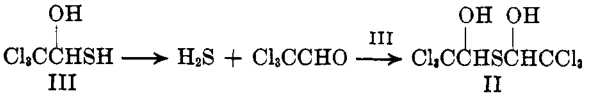


$$\mathrm{H_2S + Cl_3CCHO \xrightarrow[\text{room temp.}]{\text{sealed tube}} Cl_3C\overset{OH}{C}HSH + Cl_3C\overset{OH}{C}HS\overset{OH}{C}HCCl_3} \qquad (3a)$$

III II



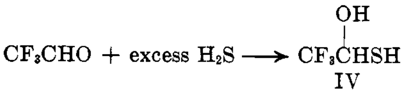
$$\mathrm{Cl_3C\overset{OH}{C}HSH + Cl_3CCHO \longrightarrow Cl_3C\overset{OH}{C}HS\overset{OH}{C}HCCl_3} \qquad (3b)$$



$$\mathrm{Cl_3C\overset{OH}{C}HSH \longrightarrow H_2S + Cl_3CCHO \xrightarrow{III} Cl_3C\overset{OH}{C}HS\overset{OH}{C}HCCl_3} \qquad (4)$$

III II

Reactions of fluorinated aldehydes with an excess of hydrogen sulfide under the conditions just described for chloral leads to the formation of 1:1 adducts in yields of 60–70%.(9) For example, trifluoroacetaldehyde and a fourfold excess of hydrogen sulfide at room temperature gave a 60% yield of the 1,1-olthiol IV (eq. 5).



$$\mathrm{CF_3CHO + excess\ H_2S \longrightarrow CF_3\overset{OH}{C}HSH} \qquad (5)$$

IV

---

(3) E. Baumann, *Ber.*, **23**, 60 (1890).

(4) H. Byasson [*ibid.*, **5**, 482 (1872)] had previously reported that the solid product obtained from chloral and hydrogen sulfide was the 1:1 adduct, but subsequent publications by E. Patterno and A. Ogialore [*Gazz. chim. ital.*, **3**, 533 (1873)], G. Wyss [*Ber.*, **7**, 211 (1874)], and H. Schiff [*ibid.*, **7**, 80 (1874)] showed that this material was actually the 2:1 adduct, $Cl_3CCH(OH)SCH(OH)CCl_3$.

(5) A. Binz, C. Räth, and E. Walter, *ibid.*, **57**, 1398 (1924).

(6) R. W. Borgeson and J. A. Wilkinson, *J. Am. Chem. Soc.*, **51**, 1453 (1929).

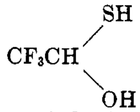
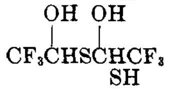
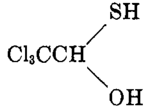
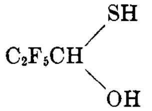
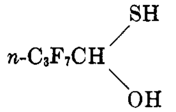
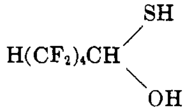
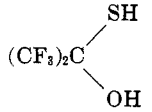
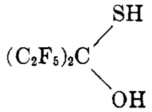
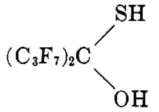
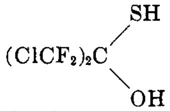
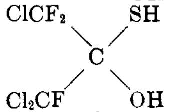
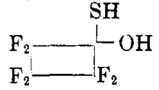
(7) E. Campaigne and B. E. Edwards, *J. Org. Chem.*, **27**, 3760 (1962).

(8) F. Asinger, M. Thiel, and G. Lipfert, *Ann.*, **627**, 195 (1959).

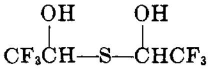
(9) At higher temperatures, *e.g.*, 200°, reductive thiolation occurs, giving fluoroalkyl thiols: J. F. Harris and W. A. Sheppard, *J. Org. Chem.*, **26**, 354 (1961).

TABLE II

PROPERTIES OF HYDROGEN SULFIDE ADDUCTS

Compd.	B.p., °C. (mm.)	n_D (°C.)	Formula	Chlorine, %		Fluorine, %		Sulfur, %		Infrared, μ	
				Calcd.	Found	Calcd.	Found	Calcd.	Found	SH	OH
	51 (80)	1.3849 (25)	$C_2H_3F_3OS$			43.1	43.8	24.2	24.0	3.85	2.95
 $CF_3CH(OH)SCH(OH)CF_3$	82–86 (16)		$C_4H_4O_2F_6S$	Carbon/hydrogen 20.8/1.8	21.4/1.6	49.5	49.3	13.9	13.7	None	3.0
	71–74 (4.0)	1.5533 (25)	$C_2H_3Cl_3OS$	58.7	58.8			17.7	17.3	3.95	2.95
	56 (66)	1.3668 (25)	$C_3H_3F_5OS$			52.1	52.4	17.6	16.8		
	53.5–54 (46)	1.3507 (25)	$C_4H_3F_7OS$			57.3	57.5	13.8	13.6		
	69–71 (17)	1.3669 (25)	$C_5H_4F_8OS$			57.5	58.7	12.1	12.2	3.85	2.9
	33 (102)	1.3338 (24)	$C_3H_2F_6OS$			57.0	56.4	16.0	16.2	3.85	2.8
	41 (56)	1.3251 (24.5)	$C_5H_2F_{10}OS$			63.3	63.2				
	38–39 (10)		$C_7H_2F_{14}OS$			66.5	66.0	8.0	7.7		
	51 (15)	1.4208 (24)	$C_3H_2Cl_2F_4OS$	30.4	30.5	32.6	33.0	13.8	14.0	3.85	2.85
	49 (3.5)	1.4614 (26)	$C_3H_2Cl_3F_3OS$	42.7	42.9	22.8	23.0	12.9	12.1		
	47 (55)	1.3686 (25)	$C_4H_2F_6OS$			53.7	53.4	15.1	14.5	3.85	3.0 (br)

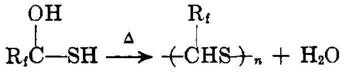
Similar results were obtained with pentafluoropropionaldehyde, heptafluorobutyraldehyde, and ω-H-octafluorovaleraldehyde (Table I). A solid hygroscopic 2:1 adduct V, analogous to the chloral–H_2S


$CF_3CH(OH)—S—CH(OH)CF_3$

V

2:1 adduct, was also obtained from a mixture of trifluoroacetaldehyde and H_2S in a 1.7:1 mole ratio. Its infrared spectrum contained a strong OH band at 3.0 μ but no SH band. Like the chloral product, it seems to be stable at room temperature indefinitely.

The 1:1 adducts obtained from fluoroaldehydes are evil-smelling, distillable liquids which exhibit characteristic OH and SH bands in the infrared spectrum. The mode of decomposition of these 1,1-olthiols is more complicated than that of the chloral adduct. After a few hours of standing at room temperature in glass containers, samples have obviously evolved some H_2S, but, on longer standing (several weeks), a second phase appears which is almost entirely water. This change may also be brought about by a few hours of reflux. The infrared spectrum of the organic phase indicated the absence of SH groups. Attempted distillation of the organic layer indicated the presence of many compounds and it seems probable that these are low polymers, cyclic and/or linear, of thioaldehydes.


$$R_fCH(OH)—SH \xrightarrow{\Delta} (CHR_fS)_n + H_2O \qquad (6)$$

Upon vacuum pyrolysis at 600° of 2,2,2-trifluoroethan-1-ol-1-thiol (IV) in a tube packed with small pieces of quartz tubing, there was obtained a purple solid at −196° which slowly lost its color on standing at this temperature. Characterization of the resulting, colorless material, which was solid at room tempera-

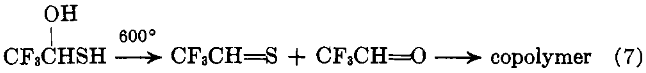
Table III

Proton N.m.r. Spectra at 60 Mc.[a]

Compd.	τ (OH)	τ (SH)	τ (CH)
$CF_3CH(OH)SH$	6.41 (J_{OH-CH} = 6.5 c.p.s.)	7.29 (J_{SH-CH} = 10 c.p.s.)	4.74
$(CF_3)_2C(OH)SH$	6.93	7.03 (J_{SH-CF_3} = 1 c.p.s.)	...
$(ClCF_2)_2C(OH)SH$	6.69	6.78 (J_{SH-CF_2} = 1 c.p.s.)	...
CF_3CH_2OH[b]	6.82	...	6.05 ($J_{CH_2-CF_3}$ = 8 c.p.s.)
$(CF_3)_2CHOH$[b]	6.99	...	5.58 (J_{CH-CF_3} = 6 c.p.s.)
$C_2F_5CH_2SH$	...	8.38 (J_{SH-CH_2} = 9 c.p.s.)	6.95 ($J_{CH_2-CF_2}$ = 15 c.p.s.)
$(C_2F_5)_2CHSH$	...	7.78 (J_{SH-CH} = 12 c.p.s.)	6.32

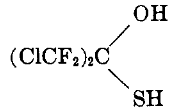
[a] Spectra were obtained with a Varian A-60 n.m.r. spectrometer using 10% solutions in carbon tetrachloride. [b] Owing to low solubility in carbon tetrachloride, this spectrum was measured in deuteriochloroform.

ture, indicated that it was a copolymer of trifluoroacetaldehyde and trifluorothioacetaldehyde with a composition corresponding to 82% thioaldehyde and 18% aldehyde. Apparently the pyrolysis caused primarily loss of the elements of water, and to a lesser extent the loss of hydrogen sulfide, to form a mixture of trifluorothioacetaldehyde, to which the purple color is apparently due, and trifluoroacetaldehyde which underwent polymerization even at −196°.[10] Analogous pyrolysis of the adduct derived from 5-H-octafluorovaleraldehyde also led to a solid copolymer with a composition corresponding to 84% thioaldehyde and 16% aldehyde.

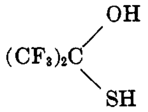


$$CF_3\overset{OH}{\overset{|}{C}}HSH \xrightarrow{600°} CF_3CH{=}S + CF_3CH{=}O \longrightarrow \text{copolymer} \quad (7)$$

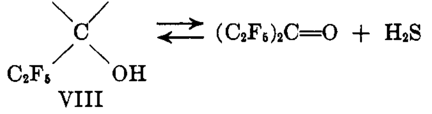
Ketones.—The formation of the H_2S adducts from *sym*-dichlorotetrafluoroacetone and hexafluoroacetone to give VI and VII was conveniently carried out at autogenous pressure and room temperature; however, better yields were obtained at 80°. These two olthiols are unique among those encountered in this study in that they appeared to be stable indefinitely at room temperature in glass vessels. In sharp contrast to this behavior was that shown by the adduct VIII from perfluoro-3-pentanone, which was completely dissociated to the ketone and H_2S after just a few hours at room temperature. The relative instability of this adduct compared to the adduct from hexafluoroacetone must be attributed to steric effects. Perfluoro-4-heptanone apparently did not react with H_2S at room temperature and autogenous pressure, but the adduct was obtained at 80° and 2000 atm. Hexafluorocyclobutanone formed a 1:1 adduct (IX) readily at room temperature and autogenous pressure, and this compound did not seem to change appreciably after several days at room temperature. An adduct was also obtained from 1,1,3-trifluorotrichloroacetone, but none was obtained when hexachloroacetone was heated with hydrogen sulfide at 80° and 2000 atm.



VI

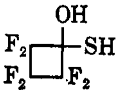


VII



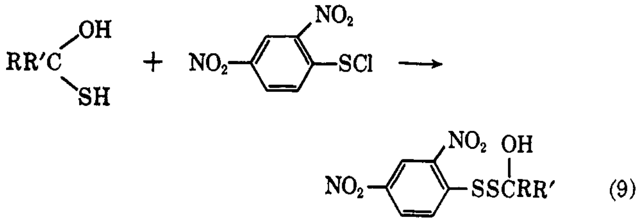
$$(C_2F_5)_2C(SH)(OH) \rightleftharpoons (C_2F_5)_2C{=}O + H_2S \quad (8)$$

VIII

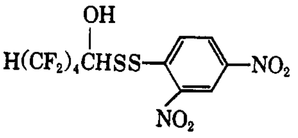


IX

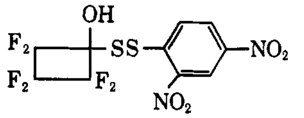
The adducts from trifluoroacetaldehyde, pentafluoropropionaldehyde, heptafluorobutyraldehyde, ω-hydroperfluorovaleraldehyde, perfluoroheptanone-4, and perfluorocyclobutanone were treated with 2,4-dinitrobenzenesulfenyl chloride in the hope of obtaining crystalline derivatives.[11] Reactions occurred in all cases, but only two of the products crystallized—those from ω-hydroperfluorovaleraldehyde and perfluorocyclobutanone. Infrared spectra indicated that the reaction which had occurred involved the SH group rather than the OH group and gave hydroxy disulfides, *e.g.*, X and XI.



(9)



X



XI

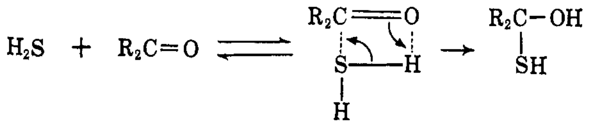
---

[10] Another example of the great ease with which fluorothioaldehydes polymerize has been observed in these laboratories: J. F. Harris and F. W. Stacey, *J. Am. Chem. Soc.*, **85**, 749 (1963). In this case the dehydrofluorination by sodium fluoride of 1,2,2-trifluoroethanethiol led to the formation of difluorothioacetaldehyde which polymerized immediately.

$$HCF_2CHFSH \longrightarrow [HCF_2CH{=}S] \longrightarrow -(\overset{HCF_2}{\overset{|}{C}}HS)-_n$$

[11] Sulfenyl halides react with both alcohols and thiols but more readily with thiols: N. Kharasch, S. J. Potempa, and H. L. Wehrmeister, *Chem. Rev.*, **39**, 269 (1946).

Both acid[2] and base[12] catalysts have been used in the reactions of carbonyl compounds with hydrogen sulfide, although it is not always clear whether the catalysis is involved in the initial addition of hydrogen sulfide to the carbonyl group, or in some later step, or both. In the reactions discussed in this paper no catalysts were intentionally added and we prefer to view the reaction simply as a nucleophilic attack by hydrogen sulfide on the carbon of the carbonyl group, perhaps occurring *via* the following steps. The relatively high order of stability of the H_2S adducts of fluorinated carbonyl compounds is, no doubt, ultimately due to the highly electronegative fluoroalkyl groups which hinder the leaving of a thiol or a hydroxyl group with its pair of electrons.



N.m.r. Spectra.—The proton n.m.r. spectra of three of the H_2S adducts together with several reference compounds are tabulated in Table III. The OH proton resonances are seen to fall in the region expected by comparison with fluorinated alcohols of similar structure. The SH resonances, on the other hand, are at somewhat lower field than in analogous fluorinated thiols. In all cases observed, the SH proton resonance is spin coupled to the α-hydrogens, or, if there are none, to the β-fluorines. Splitting of the OH is observed only in the trifluoroacetaldehyde–H_2S adduct. In no case was spin–spin coupling of the OH with the SH proton observed.

Experimental

Reactions of Aldehydes and Ketones with Excess Hydrogen Sulfide. A. Autogenous Pressure.—All of these reactions were carried out in approximately the same way. The details of each of the reactions are given in Table I. A description of the reaction with chloral follows.

A mixture of 7.5 g. (0.058 mole) of chloral and 15 g. (0.44 mole, 15 ml. at −76°) of hydrogen sulfide, which had been dried by passage through phosphorus pentoxide, was charged into an 80-ml. stainless steel pressure vessel and allowed to stand at room temperature for 18 hr. There was thus obtained a mixture of solid and liquid. The liquid was decanted, and the residue was extracted with methylene chloride. The solid weighed 1.39 g. (17%), melted at 126–131°, and was shown by infrared spectroscopy to be the 2:1 chloral–H_2S adduct previously described.[4] The liquid phase and methylene chloride extracts were combined and distilled through a small Vigreux still. There was obtained 3.62 g. (39%) of 1-hydroxy-2,2,2-trichloroethanethiol (III) distilling at 62° (2.0 mm.), n^{24}_{D} 1.5497–1.5498.

B. Atmospheres (2000–3000).—In these experiments the carbonyl compound was charged into an 80-ml. Hastelloy-C-lined shaker tube. The tube was then cooled to −76° and evacuated, and hydrogen sulfide was pressured in until the entire system was filled with liquid hydrogen sulfide. Methylcyclohexane was then pressured mechanically into the reservoir portion of the system until a pressure, calculated to result in a final pressure on the system of 2000–3000 atm. at the reaction temperature, was reached. The tube was heated to the desired temperature and then cooled, the pressure was released, and the excess hydrogen sulfide was allowed to evaporate. The olthiols were obtained by distillation of the residue.

***Preparation of* Bis(1-hydroxy-2,2,2-trifluoroethyl) Sulfide.**—A mixture of 10 ml. (at −76°, 15.5 g., 0.158 mole) of trifluoroacetaldehyde and 3.0 ml. (at −76°, 3.0 g., 0.0937 mole) of hydrogen sulfide was loaded into a small stainless steel pressure vessel and allowed to stand at room temperature overnight. The resulting mixture of solid and liquid was transferred to a flask with the help of an ether rinse and then distilled quickly through a Vigreux still. There was thus obtained 6.31 g. (35%) of product distilling at 45–59° (2–2.5 mm.), which crystallized in the receiver. A more careful distillation in another experiment gave a boiling point of 82–86° (16 mm.). The infrared spectrum contained a strong OH band at 3.0 μ but none in the region expected for a thiol group.

Decomposition of 1-Hydroxy-2,2,2-trichloroethanethiol (III).—A 1.77-g. sample of the 1:1 chloral–H_2S adduct (III) was placed in a vial and allowed to stand at room temperature. After just a few minutes the sample became cloudy. After 1 day there was a considerable quantity of solid present. The hydrogen sulfide, which had built up pressure within the vial, was released. On each succeeding day more solid was noted and the H_2S pressure was released. At the end of 10 days, the sample was entirely a dry solid and weighed 1.61 g. (100%), m.p. 123–128°. After one recrystallization from a mixture of 1.5 ml. of ether and 15 ml. of pentane, there was obtained 0.73 g. of the 2:1 chloral–H_2S adduct melting at 137–138°[13] (gas evolution and previous softening). Infrared bands were recorded at 2.83 and 2.92 μ (OH) and at 12.17 μ (C–Cl). There were no SH bands detected.

Anal. Calcd. for $C_4H_4Cl_6O_2S$: Cl, 64.7; S, 9.8. Found: Cl, 64.5; S, 9.5.

Reaction of 1-Hydroxy-2,2,2-trichloroethanethiol with Chloral.—A 2.21-g. sample of the 1:1 chloral–H_2S adduct (III) and 1.2 ml. of freshly distilled chloral were mixed in a small flask and allowed to stand at room temperature. After 0.5 hr., solid began to appear and after an additional 2 hr. the mixture was completely solid (4.12 g., m.p. 123–126°). An infrared spectrum showed that this material was the 2:1 chloral–H_2S adduct, slightly impure.

Pyrolysis of 1-Hydroxy-2,2,2-trifluoroethanethiol at Reflux.—1-Hydroxy-2,2,2-trifluoroethanethiol (16.38 g.) was heated at reflux for 18.5 hr. The mixture was cooled to room temperature, and the layers were separated. The upper layer, 1.8 ml., was shown by infrared spectroscopy to be chiefly water. There were also small quantities of fluorine-containing substances present. The organic layer, 11.81 g., contained water, but no SH compounds were apparent from infrared spectroscopy. During a distillation of this material decomposition occurred, and no pure fractions were obtained.

High Temperature Pyrolysis of 1,1-Olthiols. A. 1-Hydroxy-2,2,2-trifluoroethanethiol.—1-Hydroxy-2,2,2-trifluoroethanethiol (2 ml.) was passed during 10 min. through a 1 in. × 1 ft. quartz tube packed with small pieces of quartz tubing and heated at 600°. The exit of the pyrolysis tube was connected first to an acetone–Dry Ice cooled trap and then to a liquid nitrogen cooled trap. The entire system was maintained at a pressure of about 0.1 mm. Under these conditions, the bulk of the product condensed in the liquid nitrogen cooled trap. The condensate was initially purple, but the color soon faded. After being allowed to warm to room temperature, the isolated polymer was dried in a vacuum oven overnight at room temperature; weight 1.0 g. This material was extracted with acetone, redried, and then pressed at 75° (15,000 lb.) to an elastic, colorless opaque film. An analysis indicated that the polymer consisted of 82% trifluorothioacetaldehyde and 18% trifluoroacetaldehyde.

Anal. Calcd. for $(CF_3CHS)_{0.82}(CF_3CHO)_{0.18}$: F, 51.5; S, 23.1. Found: F, 50.9; S, 23.0.

B. 1-Hydroxy-1,5-dihydrooctafluoropentane-1-thiol.—A sample (5.09 g.) of this olthiol was pyrolyzed as described in A except that a temperature of 500° was employed. Apparently only water and hydrogen sulfide condensed in the liquid nitrogen cooled trap. The contents of the acetone–Dry Ice cooled trap were washed with chloroform and then dried overnight in a vacuum oven. Elemental analysis of the resulting polymer indicated that it was composed of 5-H-octafluorothiovaleraldehyde and 5-H-octafluorovaleraldehyde in a ratio of about 84:16.

Anal. Calcd. for $[H(CF_2)_4CHS]_{0.84}[H(CF_2)_4CHO]_{0.16}$: F, 62.4; S, 10.9. Found: F, 60.9; S, 10.9.

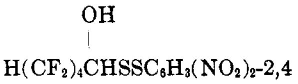
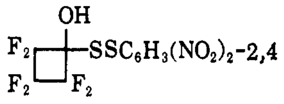
Reactions with 2,4-Dinitrobenzenesulfenyl Chloride.—These

---

(12) R. Mayer, G. Hiller, M. Nitzschke, and J. Jentzsch, *Angew. Chem., Intern. Ed. Engl.*, **2**, 370 (1963).

(13) Previously reported to melt at 138–139° by F. D. Chattaway and E. G. Kellett [*J. Chem. Soc.*, 2908 (1929)].

TABLE IV

Compd.	M.p., °C.	Infrared, μ	Formula	Calcd., % C	Calcd., % H	Calcd., % S	Found, % C	Found, % H	Found, % S
 $\mathrm{H(CF_2)_4\overset{OH}{C}HSSC_6H_3(NO_2)_2\text{-}2,4}$	93–94	2.9 (OH)	$C_{11}H_6F_8N_2O_5S_2$	28.6	1.3	13.9	28.4	1.5	14.0
	Dec. over a wide range	2.9 (OH)	$C_{10}H_4F_6N_2O_5S_2$	29.3	1.0	27.8	29.5	1.1	27.8

reactions were carried out by mixing equimolar amounts of the adduct and 2,4-dinitrobenzenesulfenyl chloride in ether, allowing the mixture to stand for a period of 0.5–18 hr., evaporating the mixture to dryness, and recrystallizing the product from carbon tetrachloride. The properties of the two crystalline derivatives obtained are given in Table IV.

The Preparation of α,α-Dichloro Ketones[1]

SAMUEL F. REED, JR.[2]

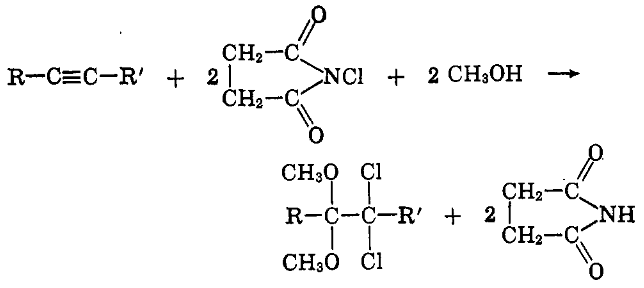
Rohm and Haas Company, Redstone Arsenal Research Division, Huntsville, Alabama

Received December 7, 1964

A novel method for the preparation of α,α-dichloro ketones has been found involving the reaction of acetylenes with N-chlorosuccinimide in methanol to give the dihalodimethyl ketals which are readily hydrolyzed with dilute acid to the ketones. The scope of the reaction appears to be of a general nature giving the ketones in 60–80% yields. The products were characterized by their proton n.m.r. spectra.

The preparative methods for the synthesis of α,α-dihalo ketones have been concerned primarily with the dihalomethyl phenyl ketones[3] and few attempts to obtain these dihalo-substituted ketones in the aliphatic series have been reported. Blaise[4] has reported on the aqueous chlorination of methyl ethyl ketone yielding 1,1-dichlorobutanone-2 and 3,3-dichlorobutanone-2 along with other products. 1,1-Difluorohexanone-2[5] has been prepared by treating N,N-diethyl-2,2-difluoroacetamide with butyllithium. Hennion and co-workers found that the chlorination of 1-hexyne in methanol[6] or water[7] yielded 1,1-dichlorohexanone-2 and other products. This reaction was extended to the chlorination of vinylacetylene in methanol[8] to give a low yield of 1,1,4-trichlorobutanone-2; however, no further extension of this reaction has been reported. More recently Wyman and Kaufman[9] have found that ketones may be chlorinated by sulfuryl chloride to give mixtures of α-chloro, α,α′-dichloro, and α,α-dichloro ketones with the latter predominating. Of the reactions discussed only the latter two appear to offer promise of being sufficiently general in scope to apply to the preparation of α,α-dichloro ketones.

In the present study it was found that acetylenes react in methanol with N-chlorosuccinimide (NCS) to yield α,α-dichlorodimethyl ketals in good yields. The reaction has been found to occur with a wide variety of acetylenes to give the one major product in all instances except with unsymmetrically disubstituted acetylenes, in which case a mixture of two dichlorodimethyl ketals is formed. For instance the reaction



R = alkyl, aryl
R′ = alkyl, hydrogen

with 2-pentyne gave both 2,2-dichloro-3,3-dimethoxypentane and 2,2-dimethoxy-3,3-dichloropentane in almost equal quantities. A mixture of 2,2-dichloropentanone-3 and 3,3-dichloropentanone-2 is obtained upon hydrolysis. Other acetylenes examined include propyne, 1-butyne, 2-butyne, 1-pentyne, 1-hexyne, 3-hexyne, and phenylacetylene.

The reactions occur readily at room temperature to give slight exotherms which may require external cooling. In general, a large excess of methanol is employed with ratios of NCS to the acetylene of 2:1. An excess of the acetylene (2:1 to 5:1) had no effect on the reaction since the dichloro ketals were isolated as the only major product. Gas chromatography studies of the crude mixtures indicated the ketals to represent 90–95% of the total products. The minor products were not characterized; however, the presence of the dichloro ketone was established as one of the minor components by its v.p.c. retention time. Its presence is attributed to slight hydrolysis of the ketal during the latter's isolation. The ketals were isolated by distillation with the exception of that obtained from

---

[1] This work was sponsored by the U. S. Army under Army Ordnance Contract DA-01-021 ORD-11878.

[2] Rohm and Haas Co., Box 672, Deer Park, Texas.

[3] (a) S. G. Cohen, H. T. Wolosinski, and P. J. Scheuer, *J. Am. Chem. Soc.*, **71**, 3439 (1949); (b) M. Prober, *ibid.*, **75**, 968 (1953); (c) L. K. Frevel and J. W. Hedelund, U. S. Patent 2,735,868 (Feb. 21, 1956); (d) F. Kröhnke, *Chem. Ber.*, **83**, 50 (1950); (e) F. Kröhnke and K. Ellegast, *ibid.*, **86**, 1556 (1953); (f) E. Rothstein and R. W. Saville, *J. Chem. Soc.*, 1961 (1949); (g) M. S. Kharasch and I. S. Bengelsdorf, *J. Org. Chem.*, **20**, 1356 (1955).

[4] E. E. Blaise, *Bull. soc. chim. France*, **15**, 728 (1914).

[5] N. A. Zaitseva, E. M. Panov, and K. A. Kocheshkov, *Izv. Akad. Nauk. SSSR, Otd. Khim. Nauk*, 831 (1961); *Chem. Abstr.*, **55**, 23301*i* (1961).

[6] J. J. Verbanc and G. F. Hennion, *J. Am. Chem. Soc.*, **60**, 1711 (1938).

[7] R. O. Norris, R. R. Vogt, and G. F. Hennion, *ibid.*, **61**, 1460 (1939).

[8] A. A. Baum, R. R. Vogt, and G. F. Hennion, *ibid.*, **61**, 1458 (1939).

[9] D. P. Wyman and P. R. Kaufman, *J. Org. Chem.*, **29**, 1956 (1964).