5.99, 6.10, 6.18, 11.2 μ. *Anal.* Found: C, 66.74; H, 6.71, and 16-methyl-9α-fluoro-1,4,15-pregnatriene-11β,17α,21-triol-3,20-dione 21-acetate (VIII), m.p. 242–247°; $[\alpha]_D^{C_3H_6O}$ +45°; $\lambda_{max}^{CH_3OH}$ 238 mμ (15,100); λ_{max}^{Nujol} 2.91, 3.05, 5.75, 5.81, 6.01, 6.15, 6.19, 11.25 μ. *Anal.* Found: C, 66.72; H, 7.08. Extended reaction of the 16β-methyl-16α,17α-oxide (V) with hydrogen chloride in acetic acid led to the 16-methylene compound (VII) and two substances evidently derived from the Δ^{15}-16, methyl compound (VIII).[8] These are, respectively-9α-fluoro-16-methyl-1,4,14,16-pregnatetraene-11,21-diol-3,20-dione 21-acetate (IX), m.p. 282–285° dec. $[\alpha]_D^{CHCl_3}$ +531°; $\lambda_{max}^{CH_3OH}$ 307 mμ (12,400), 236 mμ (16,200). *Anal.* Found: C, 69.48; H, 6.88, and 9α-fluoro-15α-chloro-16-methyl-1,4,16-pregnatriene-11,21-diol-3,20-dione 21-acetate (X), m.p. 272–275° dec. $\lambda_{max}^{CH_3OH}$ 241 mμ (20,800); $\lambda_{max}^{CHCl_3}$ 2.77, 2.90–2.95 (11β-OH), 5.74 μ (21-OAc), 6.00 μ (3,20-C=O), 6.12, 6.18, 11.16 μ.

The biological properties of the pertinent new compounds are currently being evaluated.

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Received August 1, 1960

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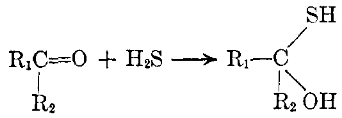
(8) Compare (5).

Hydrogen Sulfide Adducts of Halogenated Aldehydes and Ketones

Sir:

gem-Diols (aldehydes and ketone hydrates) derived from aldehydes and ketones with strong electron attracting groups—*e.g.*, chloral, bromal, glyoxylic acid, and highly fluorinated aldehydes and ketones—have been isolated and characterized. In recent years, a variety of *gem*-dithiols have been prepared and they appear to be a relatively stable class of compounds.[1,2] Apparently there is no previous report of the isolation of a compound with a hydroxyl and mercapto group on the same carbon.[3]

It has now been found that such compounds can be prepared by the reaction of hydrogen sulfide, without added catalyst, with fluorinated or chlorinated aldehydes and ketones:



$$R_1\underset{\displaystyle R_2}{\underset{|}{C}}=O + H_2S \longrightarrow R_1-\overset{\displaystyle SH}{C}(R_2)OH$$

R_1 = fluoroalkyl, fluorochloroalkyl
chloroalkyl
R_2 = fluoroalkyl
fluorochloroalkyl, H

For example, 1,3-dichloro-1,1,3,3-tetrafluoro-2-mercapto-2-propanol (b.p. 51°/15 mm., n_D^{24} 1.4208, $\lambda_{max}^{CHCl_3}$ 3.85 μ (sulfhydryl), 2.85 μ (hydroxyl), [*Anal.* Calcd. for $C_3H_2Cl_2F_4OS$: Cl, 30.4; F, 32.6; S, 13.8. Found: Cl, 30.5; F, 33.0; S, 14.0] was prepared in 91% yield by heating *sym*-dichlorotetrafluoroacetone with an excess (six-fold) of hydrogen sulfide in an autoclave at 80° for several hours. A lower yield was obtained from a comparable experiment at room temperature. The corresponding olthiols were also prepared from chloral, trifluoroacetaldehyde, pentafluoropropionaldehyde, heptafluorobutyraldehyde, 5-hydrooctafluorovaleraldehyde, decafluoro-3-pentanone, and tetradecafluoro-4-heptanone. The boiling points and refractive indices of these compounds are tabulated in Table I. All of these olthiols could be distilled *in vacuo.* The infrared spectra exhibited characteristic OH and SH frequencies. α-Hydroxy disulfides could be prepared by reaction of the olthiols with sulfenyl chlorides.

TABLE I

PROPERTIES OF OLTHIOLS, $R_1R_2C(OH)SH$

R_1	R_2	B.P./mm.	n_D^{25}
CCl_3	H	71–74/4	1.5533
CF_3	H	51/80	1.3879
C_2F_5	H	56/66	1.3611
C_3F_7	H	54/46	1.3507
$H(CF_2)_4$	H	69–71/17	1.3669
C_2F_5	C_2F_5	41/56	1.3251
C_3F_7	C_3F_7	38–39/10	—

A considerable variation in stability at room temperature was noted within this group of compounds. The olthiol derived from *sym*-dichlorotetrafluoroacetone appeared to be unchanged after several days at room temperature. The olthiol from decafluoro-3-pentanone, on the other hand, was completely decomposed, presumably to the ketone and hydrogen sulfide, after just a few hours at room temperature. Those derived from chloral and the fluorinated aldehydes are of intermediate stability.

Work is continuing to determine the scope of the H_2S— carbonyl addition reaction. A study is also being made of the chemistry of these new olthiols.

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Received September 7, 1960

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