REACTIONS OF PERFLUORODIMETHYLKETENE WITH ALCOHOLS, AMINES, AND ACIDS

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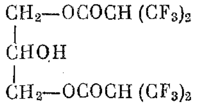
In preceding communications of this series, those reactions of perfluorodimethylketene have been described which were either completely unknown or which distinguish it from other ketenes. Such reactions include those with dimethylformamide [1], with derivatives of nitrous acid [2], and with triethyl phosphite [3], dimerization [4], and others.

In the present work we have studied the reaction of perfluorodimethylketene with alcohols, amines and acids. These reactions are general both for perfluorodimethylketene and for other, non-fluorinated ketenes and lead to the production of various derivatives of hexafluoroisobutyric acid. Thus, the reaction of the ketene with alcohols has given the esters (I)-(VI)

$$(CF_3)_2C = CO + ROH \rightarrow (CF_3)_2CH - COOR$$

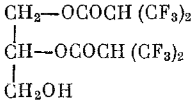
$R = CH_3$ (I); C_2H_5 (II); $i\text{-}C_3H_7$ (III); $n\text{-}C_4H_9$ (IV);
$C_3H_5O_3$ (V); $OCH(CH_2O)_2$ (VI)

It is an interesting fact that at room temperature the ketene acylates only two hydroxy groups of glycerol, giving either (Va), or (Vb)



$CH_2{-}OCOCH(CF_3)_2$ | $CHOH$ | $CH_2{-}OCOCH(CF_3)_2$

(Va)



$CH_2{-}OCOCH(CF_3)_2$ | $CH{-}OCOCH(CF_3)_2$ | CH_2OH

(Vb)

Complete acylation was achieved only by heating glycerol with an excess of perfluorodimethylketene in a sealed tube.

The reaction of the ketene with ammonia and amines has given amides of hexafluoroisobutyric acid (VII-X)

$$(CF_3)_2C{=}CO + NHR_1R_2 \rightarrow (CF_3)_2CHCONR_1R_2$$

$R_1R_2{=}H$ (VII); CH_3 (VIII); C_2H_5 (IX); H,  (X)

In the reaction of the ketene with amines, an excess of the latter must be avoided, since otherwise mineralization of the fluorine atoms takes place as a consequence of the splitting out of hydrogen fluoride from the $(CF_3)_2CH$- group, a fact previously known for similar compounds [5].

Perfluorodimethylketene readily reacts with hydrogen chloride or bromide and with organic acids, giving the acid halides (XI), (XII), the mixed anhydrides (XIII), (XIV), and the anhydride (XV).

$$(CF_3)_2C = CO + HX \rightarrow (CF_3)_2CH - COX$$

$X = Cl$ (XI); Br (XII); $OCOCF_3$ (XIII); $OCOCH_3$ (XIV);
$OCOCH(CF_3)_2$ (XV)

The properties of the compounds obtained are given in Table 1; the structures of the new compounds were confirmed by IR and NMR spectra. Identification of the known liquid substances (I), (II), and (XI) with authentic samples was carried out by the GLC method, and that of the solid substances (VII) and (VIII) by the absence of a depression of the melting point when they were mixed with authentic samples. In all other cases in which reactions gave known substances, their constants did not differ from those reported.

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TABLE 1

Cpd. No.	Yield, %	B.p. (m.p.), °C/p, mm Hg	n_D^{20}	IR spectrum, cm^{-1}	Found %	Calculated %	Reference
I	81	89—91/750	1.3072				[6]
II	79	103—105	1.3170				[6]
III	72	38/36	1.3213	1760 (CO)	C 35.2; H 3.38	C 35.2; H 3.36	
IV	90	47—49/18	1.3388	1760 (CO)	C 38.2; H 4.14	C 38.1; H 3.97	
V	43	134/10	1.3500	1770 (CO) 3570 (OH)	C 29.0; H 1.65	C 29.4; H 1.78	
VI	43	142—143/8	1.3448		C 28.7; H 1,32	C 28.7; H 1.27	
VII	46	(154—155)					[6]
VIII	44	(54—55)					[7]
IX	37	(50.5)					[6]
X	55	(185—186)		1580. 1650 1672 (CO)	C 43.5; H 4.80; N 5.33	C 43.4; H 4.69; N 5.06	
XI	54	54/748	1.3080				[8]
XII	79	66—67/748					[8]
XIII	26	132—133	1.3055	1785 1856 (CO)	C 24.9: H 0.80; F 58.5	C 24.6; H 0.34; F 58.6	
XIV	83	142	1.3289	1780. 1852 (CO)	C 30.1; H 1.66; F 47.8	C 30.2; H 1,68; F 47.9	
XV	74	135—137	1.3100				[9]

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*The NMR spectra were taken in CCl_4 with Me_4Si as internal standard. (IV) δCH_3 0.95(triplet), J 5.6 c/s; δOCH_2 4.30(triplet); δCH 4.13 (septet), J 8.0 c/s; $\delta C-CH_2$ 1.3-1.6(multiplet). (III) δCH_2 1.3(doublet), J 6.2 c/s; δOCH 5.2(septet); δCCH 4.1(septet), J 7.5 c/s.

EXPERIMENTAL

Methyl and Ethyl Alcohols. Perfluorodimethylketene was passed into an excess of the alcohol, and then the mixture was diluted with water and the oil which separated was washed with bicarbonate solution and with water and was dried and distilled.

Isopropyl and Butyl Alcohols. Equimolar amounts of alcohol and the ketene were mixed in a tube at −78°, left for a day at room temperature, and then treated as described above.

Glycerol. Glycerol was placed in a two-necked flask with a reflux condenser cooled to −78°, and the ketene was passed through it until absorption ceased. Then the product was treated in a similar manner to that described above. The ester (V) was obtained.

A mixture of the ester (V) and an excess of perfluorodimethylketene was heated in a sealed tube for 6 h at 100°. The product was treated similarly. This gave the ester (VI).

Ammonia and Dimethylamine. At −78°, an equimolar amount of ammonia or an amine was passed into an ethereal solution of the ketene in a two-necked flask. The resulting mixture was heated under reflux to room temperature. Then the ether was evaporated in the air, and the residue was crystallized from heptane.

Diethylamine, Cyclohexylamine. In drops, an equimolar amount of the amine was added to an ethereal solution of the ketene in a flask with a reflux condenser at −78°. The subsequent treatment was as described above. The amides were crystallized from benzene or alcohol.

Hydrogen Chloride. The ketene, placed in a two-necked flask with a reflux condenser (−78°), was saturated with dry HCl at room temperature for 5 h. The product was distilled through a column.

Other Acids. Equimolar amounts of the ketene and HBr or other acids were sealed in a tube and left for a day. After this, the acid bromide (XII) was distilled through a column, and the anhydrides (XIII)-(XV) were carefully washed with ice water and bicarbonate solution, dried, and distilled.

CONCLUSIONS

Perfluorodimethylketene is a good acylating agent for alcohols and amines and both mineral and organic acids.

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