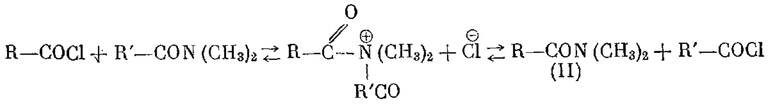
REACTIONS OF CARBOXYLIC ACID CHLORIDES WITH DIMETHYLFORMAMIDE

I. L. Knunyants, Yu. A. Cheburkov,
and Yu. E. Aronov

UDC 542.95 + 542.951

The reactions of dimethylformamide (DMFA) with organic acid chlorides have received little study. It is known only that benzoyl chloride (Ia) reacts with DMFA under relatively severe conditions (at the boil) with formation of N,N-dimethylbenzamide (IIa) [1]. This reaction really amounts to transamidation, which in principle can be effected as an equilibrium reaction for any pair made up of a disubstituted amide and a carboxylic acid chloride [2]

Scheme 1



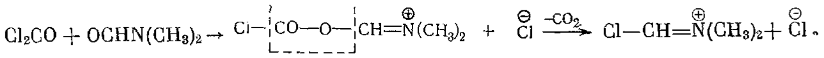
$$R{-}COCl + R'{-}CON(CH_3)_2 \rightleftarrows R{-}\overset{O}{\overset{/\!/}{C}}{-}\overset{\oplus}{\underset{\substack{|\\ R'CO}}{N}}(CH_3)_2 + \overset{\ominus}{Cl} \rightleftarrows R{-}\underset{(II)}{CON}(CH_3)_2 + R'{-}COCl$$

(I) (II)

$R' = H$; R: a = C_6H_5; b = CH_3; c = CF_3; d = $(CH_3)_2CH$; e = C_3F_7;
k = CCl_3.

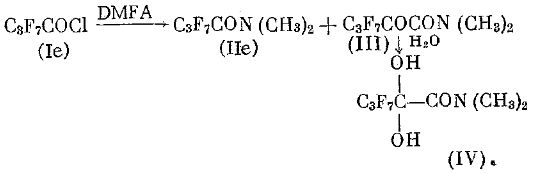
When DMFA (R' = H) is taken as the disubstituted amide, one of the partners in the equilibrium becomes the unstable formyl chloride, which decomposes irreversibly into carbon monoxide and hydrogen chloride; the reaction therefore goes in the forward direction to completion. In scheme 1 the first act of the reaction is attack by the electrophilic carbon atom of the carbonyl group of the acid chloride on the nitrogen atom of DMFA.

It is known that in the first stage of the Vilsmeier-Haack reaction [3] phosgene [4], carbonyl fluoride [5], and oxalyl chloride [6] react with DMFA in such a way that attack by the electrophilic species $R\overset{\oplus}{C}O$ (in which R = Cl, F, COCl) is directed on the oxygen atom of DMFA. An unstable adduct is formed, and its decarboxylation leads to the corresponding methyleneammonium salt:



$$Cl_2CO + OCHN(CH_3)_2 \rightarrow Cl{-}CO{-}O{-}CH{=}\overset{\oplus}{N}(CH_3)_2 + \overset{\ominus}{Cl} \xrightarrow{-CO_2} Cl{-}CH{=}\overset{\oplus}{N}(CH_3)_2 + \overset{\ominus}{Cl}.$$

We have investigated the reactions of carboxylic acid chlorides with DMFA, and we have found a number of examples which enable us to propose a general scheme for the reactions of organic acid chlorides with DMFA. It was found that, like benzoyl chloride (Ia), acetyl (Ib), trifluoroacetyl (Ic), isobutyryl (Id), and heptafluorobutyryl (Ie) chlorides react with DMFA with formation of the corresponding N,N-dimethylalkanamides (IIb)-(IIe) (see scheme 1). In the case of heptafluorobutyryl chloride (Ie), as well as the main product (IIe), heptafluoro-N,N-dimethyl-2-oxovaleramide (III) is formed:



$$\underset{(Ie)}{C_3F_7COCl} \xrightarrow{DMFA} \underset{(IIe)}{C_3F_7CON(CH_3)_2} + \underset{(III)}{C_3F_7COCON(CH_3)_2} \xrightarrow{H_2O} C_3F_7\overset{OH}{\underset{OH}{C}}{-}CON(CH_3)_2$$

(IV).

The structure of (III) was confirmed by its IR spectrum (two carbonyl absorption bands) and its F^{19} NMR spectrum, in which the signal from the CF_3 group is split into a triplet as a result of the spin-spin interaction between the fluorine atoms of the CF_3 and β-CF_2 groups. Such a character in the spin-spin interaction is in accord with the F^{19} NMR spectrum of the C_3F_7 group [7] and is analogous to that found in the

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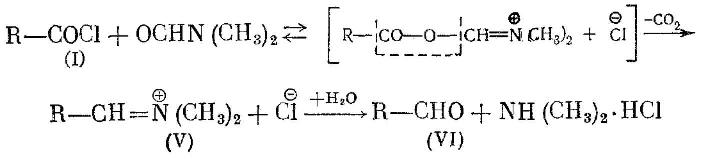
Institute of Heteroorganic Compounds, Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 6, pp. 1038-1047, June, 1966. Original article submitted December 7, 1965.

spectrum of the dimethylamide (IIe). The structure (III) was also confirmed by the formation of the hydrate (IV). The mechanism of the formation of (III) will be investigated. Unlike the acid chlorides enumerated above, which react in accordance with scheme 1, 3,3,3-trifluoro-2-(trifluoromethyl)propionyl chloride (If) reacts with DMFA under mild conditions with liberation of carbon dioxide and formation of an unstable crystalline substance, which is readily hydrolyzed into the known [8] 3,3,3-trifluoro-2-(trifluoromethyl)-propionaldehyde (VIf) (scheme 2). This result is readily explained if we assume that in this reaction, as in the above-cited reaction for phosgene, the initial attack of the electrophilic carbon atom of the carbonyl group of the acid chloride is directed onto the oxygen atom of DMFA, which leads to the formation of a salt which is decarboxylated into dimethyl[3,3,3-trifluoro-2-(trifluoromethyl)propylidene]ammonium chloride (Vf), which is hydrolyzed to the aldehyde (VIf).

Scheme 2



$$\underset{(I)}{R{-}COCl} + OCHN(CH_3)_2 \rightleftarrows \left[R{-}CO{-}O{-}CH{=}\overset{\oplus}{N}(CH_3)_2 + \overset{\ominus}{Cl}\right] \xrightarrow{-CO_2}$$

$$\underset{(V)}{R{-}CH{=}\overset{\oplus}{N}(CH_3)_2} + \overset{\ominus}{Cl} \xrightarrow{+H_2O} \underset{(VI)}{R{-}CHO} + NH(CH_3)_2\cdot HCl$$

R: f $= (CF_3)_2CH$; g $= (CF_3)_2CCl$; h $= (CF_3)_2CBr$; i $= (CF_3)_2C(CH_3)$;
j $= (CF_3)_3C$; k $= CCl_3$

Further confirmation of this reaction mechanism was provided by the investigation of the IR spectrum of the alkylideneammonium salt (Vg); we succeeded in isolating this intermediate product by conducting the reaction between 2-chloro-3,3,3-trifluoro-2-(trifluoromethyl)propionyl chloride (Ig) and DMFA in diethyl ether solution. Although it was not found possible to obtain the salt (Vg) in a pure state because of the occurrence of the side processes considered below, the absorption band of the carbonyl group of the original acid chloride at 1760 cm^{-1} was quite clearly absent from its IR spectrum, and a new band appeared at 1691 cm^{-1}, characteristic for the $> C = \overset{\oplus}{N} <$ group. A product of similar structure was isolated earlier by Arnold [4] in the reaction of phosgene with DMFA.

Acid chlorides which react with DMFA in an analogous way to 3,3,3-trifluoro-2-(trifluoromethyl)-propionyl chloride (If), i.e., through the stage of decarboxylation and formation of an alkylideneammonium salt (V), are 2-chloro- (Ig) and 2-bromo- (Ih) -3,3,3-trifluoro-2-(trifluoromethyl)propionyl chlorides, 3,3,3-trifluoro-2-methyl-2-(trifluoromethyl)propionyl chloride (Ii), perfluoropivaloyl chloride (Ij), and trichloroacetyl chloride (Ik). However, the reaction is often complicated by side processes (see below), as a result of which it is not always possible to isolate the aldehyde (VI), but only its transformation products.

Apart from aldehydes, the products of the reactions of 3,3,3-trifluoro-2-(trifluoromethyl)propionyl chlorides (If), (Ig), and (Ih) and of trichloroacetyl chloride (Ik) with DMFA include the corresponding chloroalkanes (VII) and carbon monoxide — products of the decarbonylation of the original acid chlorides.

Scheme 3

$$\underset{(I)}{R{-}COCl} \xrightarrow{DMFA} \underset{(VII)}{R{-}Cl} + CO$$

R: f $= (CF_3)_2CH$; g $= (CF_3)_2CCl$; h $= (CF_3)_2CBr$; k $= CCl_3$

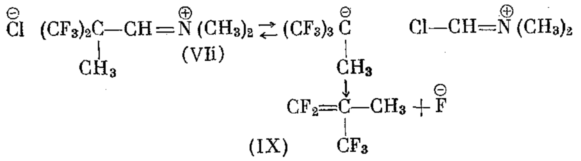
Trichloroacetyl chloride (Ik) is the only one of the acid chlorides which we investigated which reacts with DMFA in accordance with Schemes 1, 2, and 3 simultaneously, which leads to the formation of 2,2,2-trichloro-N,N-dimethylacetamide (IIk), chloral (VIk), and carbon tetrachloride (VIIk). Perfluoropivaloyl chloride (Ij) reacts with DMFA with liberation of one molecular proportion of carbon dioxide and formation of a saltlike product, which on hydrolysis gives 2H-hexafluoro-2-(trifluoromethyl)propane (VIII). This can be explained on the assumption that, under the conditions of the hydrolysis of the alkylideneammonium salt (Vj) (i.e., in aqueous DMFA at 0°), perfluoropivalaldehyde (VIj) (perfluoropivalaldehyde is unknown) is unstable and is quickly decarbonylated (see scheme on following page).

The course of the reaction of DMFA with 3,3,3-trifluoro-2-methyl-2-methyl-2-(trifluoromethyl)-propionyl chloride (Ii) is more complex. By conducting the reaction under mild conditions we were able

$$\underset{(\mathrm{Ij})}{(CF_3)_3CCOCl} \xrightarrow[-CO_2]{+DMFA} \underset{(\mathrm{Vj})}{(CF_3)_3CCH{=}\overset{\oplus}{N}(CH_3)_2} + \overset{\ominus}{Cl} \xrightarrow{+H_2O}$$

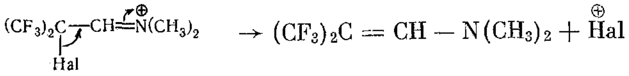
$$\to \underset{(\mathrm{VIj})}{[(CF_3)_3CCHO]} \to \underset{(\mathrm{VIII})}{(CF_3)_3CH} + CO$$

to isolate the corresponding aldehyde (VIi) after the hydrolysis, but in very low yield. Under severe conditions (in a sealed tube at 140°) the only reaction product was 2-methylpentafluoropropene (IX), whose structure follows from the IR spectrum and the character of the splitting of the signal from its protons in the NMR spectrum (triplet of a methyl group adjacent to a CF_2 group). One of the possible routes in the formation of the olefin (IX) is the rearrangement of the alkylideneammonium salt (Vi) in accordance with the scheme



The possibility of such a rearrangment has been shown earlier [8].

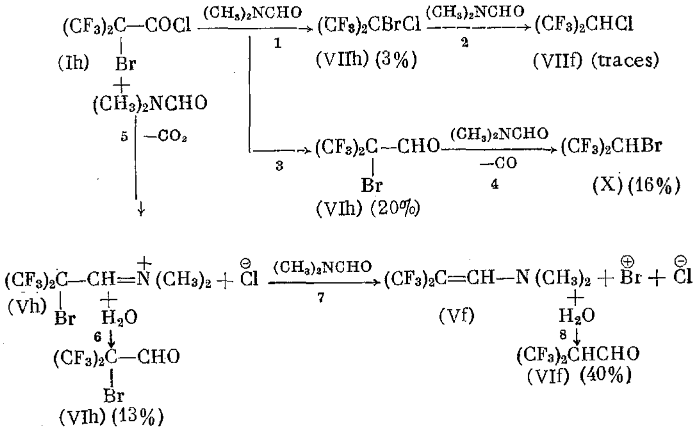
In the hydrolysis of the alkylideneammonium salts obtained from 2-chloro- and 2-bromo-3,3,3-trifluoro-2-(trifluoromethyl)propionyl chlorides (Ig) and (Ih) in each case a mixture was formed of 3,3,3-trifluoro-2-(trifluoromethyl)propionaldehyde (VIf) and the 2-halo-3,3,3-trifluoro-2-(trifluoromethyl)propionaldehyde (VIg) or (VIh), respectively, which are known substances [8]. To explain this phenomenon it must be assumed that the covalently bound halogen atom present in the ammonium salt under the influence of three powerful electron-attracting groups can be eliminated under mild conditions in the form of a cation, which halogenates the solvent.



An analogous process has been described for 2-bromo-3,3,3-trifluoro-2-(trifluoromethyl)propionic ester [9]. It is this loss of a halogen atom by the ammonium salt which made it impossible to isolate [2-chloro-3,3,3-trifluoro-2-(trifluoromethyl)propylidene]trimethylammonium chloride (Vg) in a pure state.

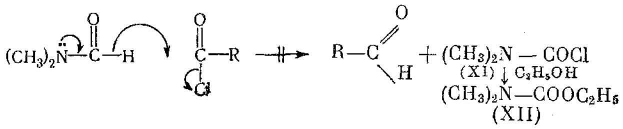
The reaction of DMFA with 2-bromo-3,3,3-trifluoro-2-(trifluoromethyl)propionyl chloride (Ih) is complicated by a large number of the side processes shown in scheme 4 (in parentheses we give the yields of the products in percent on the acid chloride taken):

Scheme 4



In accordance with the mechanism given in scheme 2 and with consideration of the above-mentioned halogenation of the solvent, in this reaction the aldehydes (VIh) and (VIf) are formed (by routes 5-6 and 5-7-8 respectively). 2-Bromo-2-chlorohexafluoropropane (VIIh) is formed by the decarbonylation of the acid chloride (Ih) (route 1). As well as these substances the reaction mixture contains 2H-2-bromohexafluoropropane (X), probably formed by the decarbonylation of the aldehyde (VIh) (route 3-4). The possibility of such a reaction was confirmed in a special experiment. Finally, 2H-2-chlorohexafluoropropane may be formed as a result of the bromination of the solvent by the bromochlorohexafluoropropane (VIIh) (route 1-2).

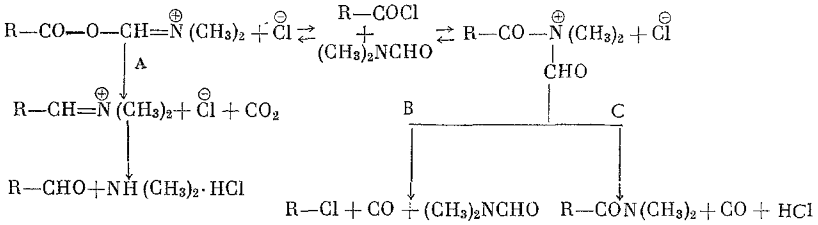
The greatest interest is presented here by the formation, only in this reaction, of 2-bromo-3,3,3-trifluoro-2-(trifluoromethyl)propionaldehyde (VIh) before the hydrolysis of the reaction mixture with possible bypassing of the stage of the formation of the ammonium salt (Vh) (route 3). We consider that in this case DMFA may play the role of the donor of a hydride ion and that the reaction of hydride transfer is responsible for the formation of the aldehyde.



However, we tried unsuccessfully to detect, by thin-layer chromatography, one of the possible transformation products from DMFA (XI) in the form of ethyl dimethylcarbamate (XII) after treatment of the reaction mixture with alcohol. Just as unsuccessful were our attempts to reduce 3,3,3-trifluoro-2-(trifluoromethyl)propionyl chloride (If) and its 2-chloro and 2-bromo derivatives (Ig) and (Ih) with such hydride-ion donors as cycloheptatriene and trialkylsilanes. Hence, the question of the possibility in this case of the direct reduction of the acid chloride (Ih) with dimethylformamide remains open.

From the experimental material reported it follows that in a solution of a carboxylic acid chloride in DMFA two types of salts are present simultaneously: they are formed as a result of attack by the electrophilic center of the acid chloride on the oxygen of DMFA, in the one case, and on the nitrogen of DMFA, in the other.

Scheme 5



If an acid chloride in which, because of structural peculiarities, the R—C bond is weakened is brought into reaction with DMFA, there occurs decarboxylation (route A) or decarbonylation (route B) of the corresponding salts (formed by the acid chloride with DMFA) with formation of the aldehyde or the chloroalkane. It should be noted that both these processes occur with acid chlorides of those acids which are themselves fairly readily decarboxylated. If, however, into reaction with DMFA we bring the acid chloride of a nondecarboxylating acid, then under more severe conditions transamidation occurs with formation of the dimethylamide of the corresponding acid (route C). The previously described reactions of the acid chlorides of the readily decarboxylated carbonic and oxalic acids (route A) [4-6] and the nondecarboxylating benzoic acid (route C) with DMFA also fit into the proposed scheme. The main results of the investigation are given in Table 1. As the yield in reactions by route A is to be understood the yield of the corresponding aldehyde or other substances which can be interpreted as products of the transformation of the intermediate ammonium salt or the aldehyde. For example, in the case of perfluoropivaloyl chloride (Ij) this is the yield of 2H-hexafluoro-2-(trifluoromethyl)propane (VIII); in the case of 2-chloro-3,3,3-trifluoro-2-(trifluoromethyl)propionyl chloride (Ig) this is the sum of the yields of 3,3,3-trifluoro-2-(trifluoromethyl)propionaldehyde (VIf) and its 2-chloro derivative (VIg), etc. Table 1 may be useful for the qualitative assessment of the ease with which reaction proceeds along each of the directions A, B, and C.

EXPERIMENTAL

The mixtures were analyzed and identified with known samples (the latter are given with references to the method of preparation in the text) by means of gas-liquid chromatography on at least two columns

TABLE 1

R—COCl	Yield, %, in reaction along the route			Reaction temp., °C	Reaction time
	A	B	C		
$(CF_3)_2CHCOCl$ (If)	48	17	0	30-60	1 h
$(CF_3)_2CClCOCl$ (Ig)	43	40	0	0	30 min
$(CF_3)_2CBrCOCl$ (Ih)	75	20	0	—10-0	15 min
$(CF_3)_3CCOCl$ (Ij)	67	0	0	—78	30 min
$CF_3)_2C(CH_3)COCl$ (Ii)	68	0	0	140	5 h
CCl_3COCl (Ik)	10	17	20	80	5 h
CH_3COCl (Ib)	0	0	60	153	2 h
CF_3COCl (Ic)	0	0	67	120	18 h
$(CH_3)_2CHCOCl$ (Id)	0	0	83	153	2 h
C_3F_7COCl (Ie)	0	0	62	100	45 h

with different stationary phases and of thin-layer chromatography on alumina containing 8% of moisture in 1 : 5 acetone-hexane. The compositions of the mixtures were calculated from a comparison of the areas of the corresponding peaks in gas-liquid chromatography.

Starting Substances. Dimethylformamide of "Pure" grade was dried for one day over P_2O_5 and distilled twice over P_2O_5 with collection of the fraction of b.p. 153°.

Acetyl (Ib), trifluoroacetyl (Ic), isobutyryl (Id), heptafluorobutyryl (Ie), and trichloroacetyl (Ik) chlorides were prepared in the usual way by treating the corresponding acids with phosphorus pentachloride, and they were purified by distillation through a column.

3,3,3-Trifluoro-2-(trifluoromethyl)propionyl (If) and 2-bromo-3,3,3-trifluoro-2-(trifluoromethyl)-propionyl (Ih) chlorides were prepared by the action of anhydrous aluminum chloride on the corresponding acid fluorides [10], and 2-chloro-3,3,3-trifluoro-2-(trifluoromethyl)propionyl chloride (Ig) was synthesized by the chlorination of bistrifluoromethylketene [11].

Perfluoropivaloyl Chloride (Ij). A 50-ml glass tube was charged with 10 g of anhydrous aluminum chloride and cooled to —78°; 14.9 g of perfluoropivaloyl fluoride [12] was added. The tube was sealed, and the contents were carefully mixed by shaking. The tube was heated in a boiling water bath for 3 h, and was then cooled to —78° and opened; the contents were vacuum-distilled off. By distillation of the condensate through a column with a condenser thermostated at 28° we isolated 4 g (25%) of the acid chloride (Ij), b.p. 62° (755 mm); m.p. 26.5°. Found %: Cl 12.6. C_5F_9ClO. Calculated %: Cl 12.6. IR spectrum (ν_{max}, cm^{-1}): 730 s; 750 s; 760 s; 990 s; 1070 m; 1210 m; 1275 s; 1360 m; 1575 m; 1795 v.s (C = O).

3,3,3-Trifluoro-2-methyl-2-(trifluoromethyl)propionyl Chloride (Ii). This was prepared like (Ij) from 3,3,3-trifluoro-2-methyl-2-(trifluoromethyl)propionyl fluoride [13] in 64% yield; b.p. 77-78° (749 mm); n_D^{20} 1.3298. Found %: Cl 15.8. $C_5H_3F_6ClO$. Calculated %: Cl 15.6. IR spectrum (ν_{max}, cm^{-1}): 800 m; 890 w; 950 m; 1090 s; 1160 m; 1200-13500 v.s; 1470 m; 1800 s (C = O).

Reactions of Dimethylformamide with Acid Chlorides

Typical Experiment. Two or three times the stoichiometric amount of DMFA was introduced into a three-necked flask fitted with a stirrer, a dropping funnel with a bypass tube, and a reflux condenser (in work with low-boiling acid chloride the water-cooled reflux condenser was surmounted by a reflux condenser cooled with a mixture of solid carbon dioxide and acetone) connected through a trap (—78°) with a gas holder. The flask was cooled to —78°, and the acid chloride was added dropwise with stirring. Then, if gas was not liberated, by gradual raising of the temperature suitable conditions were found for the reaction to start, and the reaction mixture was kept at this temperature until the theoretical volume of gas had been liberated (CO, CO_2, or a mixture of these).

When no more gas came off, all that would distill at a residual pressure of 5-7 mm with heating up to 50° was driven off into the same trap. The structures of unknown substances were proved with the aid of their NMR and IR spectra.

The reaction mixture was then hydrolyzed with the theoretical amount of water with cooling and was diluted further with water if this was necessary for the distillation of the aldehyde or the layer formation of the dimethylamide. After the separation of these products the aqueous-dimethylformamide solution was extracted repeatedly with ether. The ether extract was dried and concentrated and then investigated by means of gas-liquid and thin-layer chromatography.

With 3,3,3-Trifluoro-2-(trifluoromethyl)propionyl Chloride (If). The reaction [10 g of (If)] was carried out for 1 h with gradual raising of the temperature over the range 30-60°. The theoretical volume of a mixture of CO_2 and CO was liberated, and 2H-2-chlorohexafluoropropane (VIIf) was formed in 17% yield [14]. The reaction mixture was hydrolyzed and diluted with an equal volume of water, and 3,3,3-trifluoro-2-(trifluoromethyl)propionaldehyde (VIf) was distilled off (48% yield) [8]. In the ether extract the dimethylamide (IIf) was not detected.

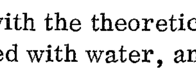
With 2-Chloro-3,3,3-trifluoro-2-(trifluoromethyl)propionyl Chloride (Ig). The reaction [13 g of (Ig)] started at 0° and went with liberation of heat. With the aid of a cooling bath the temperature was kept in the range 0-10°. Before the hydrolysis 2,2-dichlorohexafluoropropane (VIIg) was formed (40% yield) [15]. After the hydrolysis we isolated 2-chloro-3,3,3-trifluoro-2-(trifluoromethyl)-propionaldehyde (VIg) (5.5% yield) [8], 3,3,3-trifluoro-2-(trifluoromethyl)propionaldehyde (VIf) (37% yield), and 2H-2-chlorohexafluoropropane (VIIf) (less than 1%). No dimethylamides were detected in the ether extract.

With 2-Bromo-3,3,3-trifluoro-2-(trifluoromethyl)propionyl Chloride (Ih). The reaction [20 g of (Ih)] started at —10° and went to completion with cooling with ice. The products then formed were 2H-2-bromohexafluoropropane (X) (16% yield) [14], 2-bromo-3,3,3-trifluoro-2-(trifluoromethyl)propionaldehyde (VIh) (20% yield) [8], 2-bromo-2-chlorohexafluoropropane (VIIh) (3% yield) [14], and traces of 2H-2-chlorohexafluoropropane (VIIf). After the hydrolysis, which was conducted under ice cooling, and the dilution with an equal volume of water, 2-bromo-3,3,3-trifluoro-2-(trifluoromethyl)propionaldehyde (VIh) (13% yield) in admixture with the aldehyde (VIf) (41% yield) were driven from the aqueous-dimethylformamide solution. No dimethylamide was detected in the ether extract.

With 2-Bromo-3,3,3-trifluoro-2-(trifluoromethyl)propionaldehyde (VIh). A mixture of 4.5 g of (VIh) and 1.3 g of DMFA was heated in a sealed tube for 2 h at 90°. The tube was cooled and opened, the contents were diluted with water, and all that would come over at the temperature of a boiling water bath was distilled off. After drying and distillation we obtained 4.1 g of a product containing 77% of the original aldehyde (VIh) and 23% of 2H-2-bromohexafluoropropane (X).

With Perfluoropivaloyl Chloride (Ij). The reaction [0.93 g of (Ij)] was conducted at —78°. The theoretical volume of carbon dioxide was liberated. After the hydrolysis of the reaction mixture, which was conducted with cooling with ice, 2H-hexafluoro-2-(trifluoromethyl)propane (VIII) (67% yield) was driven off into a trap (—78°) [16]. No dimethylamide was detected in the ether extract.

With 3,3,3-Trifluoro-2-methyl-2-(trifluoromethyl)propionyl Chloride (Ii). The reaction with 4.8 g of (Ii) was carried out for 4 h with heating in a boiling water bath. 10% of the theoretical amount of gas was liberated, and 83% of unchanged acid chloride was recovered. After the hydrolysis of the reaction mixture 3,3,3-trifluoro-2-methyl-2-(trifluoromethyl)propionaldehyde (29% on the acid chloride that reacted) was obtained. The aldehyde was identified as its 2,4-dinitrophenylhydrazone; this had m.p. 143° after dissolution in ether and separation from unchanged 2,4-dinitrophenylhydrazine by crystallization from aqueous alcohol from a mixture of alcohol and hexane, and from CCl_4. Found %: C 35.8; H 2.3. $C_{11}H_8F_6N_4O_4$. Calculated %: C 35.3; H 2.2.

1.48 g of the acid chloride (Ii) was introduced into a 20-ml glass tube, and with cooling to —78° 2.5 g of DMFA was added. The sealed tube was heated for 5 h at 140°, and a colorless lower layer formed in the reaction mixture; the tube was cooled and opened, and this layer was readily distilled off. We obtained 1 g (68%) of a product of b.p. 9° (745 mm), which was found to be 2-methylpentafluoropropene (IX). IR spectrum (ν_{max}, cm^{-1}): 1766 (C=C); PMR spectrum relative to tetramethylsilane:  $CH_3-\underset{CF_3^2}{\underset{|}{C}}=CF_2^1$, δH 1.75 (triplet), J H—F(1) 3 Hz. The literature [17] gives b.p. 12.8°.

With Trichloroacetyl Chloride (Ik). The reaction [15 g of (Ik)] was conducted at 80° for 5 h. When the theoretical volume of a mixture of CO and CO_2 had been liberated from the reaction mixture CCl_4 (VIIk) (17% yield) was driven off; the residue was hydrolyzed with the theoretical volume of water, and chloral (VIk) was driven off (10% yield). The residue was diluted with water, and 2,2,2-trichloro-N,N-dimethylacetamide (IIk) was separated (20% yield) and identified by thin-layer chromatography with a sample prepared from the acid chloride (Ik) and dimethylamine.

With Acetyl Chloride (Ib) and with Isobutyryl Chloride (Id). Each of the acid chlorides [21.5 g of (Ib) and 10.8 g of (Id)] was refluxed with 2.5 times the theoretical amount of DMFA until the theoretical volume of CO had been liberated. In both cases a yield of about 80% of the hydrochloride of the corresponding dimethylamine (IIb) and (IId) was obtained, and from these by the action of triethylamine the dimethylamides were isolated in yields of 60 and 83% respectively. The dimethylamide (IId) was identical to the product obtained from the acid chloride (Id) and dimethylamine [18].

With Trifluoroacetyl Chloride (Ic). 7 g of (Ic) was heated with 10 g of DMFA at 120° for 18 h in a Teflon-coated autoclave. The autoclave was opened, and the theoretical volume of CO was liberated. The reaction mixture was diluted with three times its volume of water and repeatedly extracted with ether. The extract was dried and evaporated, and we isolated a 67% yield of 2,2,2-trifluoro-N,N-dimethylacetamide (IIc), identical to a sample prepared from the acid chloride (Ic) and dimethylamine [19].

With Heptafluorobutyryl Chloride (Ie). A mixture of 8.8 g of (Ie) and 5 g of DMFA was heated in a sealed tube for 20 h in a boiling water bath. The tube was cooled to —78° and opened to release the pressure which had developed, a further 4 g of DMFA was added, the tube was sealed, and heating was continued in the boiling water bath for 28 h. The tube was cooled to —78° and opened, and again a considerable pressure was revealed. The contents were diluted with twice their volume of water, the lower layer which then formed was separated, and the upper aqueous layer was extracted with ether. The oil which had been separated was combined with the ether extracts, which were then dried with calcium chloride. Ether was driven off, and the residue was distilled at 34-100° (26 mm). The distillate contained heptafluoro-N,N-dimethylbutyramide (IIe) (43% yield), identical to the substance obtained from the acid chloride (Ie) and dimethylamine [20], and an unknown substance, which was identified as heptafluoro-N,N-dimethyl-2-oxovaleramide (III) (20% yield).

To isolate (III) the mixture was fractionated through a column with separation of about 75% of the dimethylamide (IIe) present [b.p. 64° (20 mm)], and the residue was placed in a Petri dish in a desiccator containing a layer of water in the bottom. In the course of two days the liquid crystallized out completely. The crystals were washed free from (IIe) with hexane and dried in air. The substance readily loses water when heated and under the action of drying agents; it is insoluble in hydrocarbons. It was identified in the form of the dihydrate of heptafluoro-N,N-dimethyl-2-oxovaleramide (IV). Found %: C 27.8; H 3.3; F 43.6. $C_7F_7H_{10}NO_4$. Calculated %: C 27.5; H 3.3; F 43.6.

IR spectrum (ν_{max}, cm^{-1}): 740 m; 750 w; 825 w; 850 w; 920 m; 1010 m; 1085 s; 1125 v.s; 1147 v.s; 1187 v.s; 1200 v.s; 1225 v.s; 1242 v.s; 1284 v.s; 1338 m; 1358 m; 1383 m; 1467 m; 1500 w; 1644 v.s; (C=O), 2842 m; 2967 m; 3140 s; 3325 v.s; 3465-3479 v.s (OH).

When an ethereal solution of (IV) is treated with diphosphorus pentoxide in the cold it loses two molecules of water and is converted into (III), b.p. 82.5-83° (18 mm); n_D^{20} 1.3542. Found %: C 31.2; H 2.2; N 5.2. $C_7F_7H_6NO_2$. Calculated %: C 31.2; H 2.2; N 5.2. IR spectrum (ν_{max}, cm^{-1}): 1760 (C=O) and 1680 (C=O). The PMR spectrum contains a methyl singlet with δ 2.97 relative to tetramethylsilane [20]. F^{19} NMR spectrum relative to BTF: $CF_3-CF_2^1-CF_2^2-CO-CON(CH_3)_2$, δ CF_3 18.1 (split triplet) J CF_3-CF_2 (2), 8.5 Hz; $\delta CF_2(1)$ 44.5, $\delta CF_2(2)$ 37.5 (quartet).

With 2-Chloro-3,3,3-trifluoro-2-(trifluoromethyl)propionyl Chloride (Ig). 2 g of (Ig) was dissolved in 5 ml of dry ether, and 1.5 g (an excess) of DMFA was added dropwise at room temperature. All operations were conducted in a tightly closed chamber containing diphosphorus pentoxide and filled with a stream of dry nitrogen. Gas was liberated, and a white crystalline substance was precipitated. The crystals were filtered off, washed repeatedly with dry ether, and dried. From a part of the substance a suspension in mineral oil was prepared in the protective chamber for use in IR spectroscopy. IR spectrum: ν_{max} 1691 cm^{-1}. The residue was hydrolyzed with water, when a mixture of the aldehydes (VIg) and (VIf) was formed.

CONCLUSIONS

1. It is shown that the reaction between carboxylic acid chlorides and dimethylformamide can take a previously unobserved course with formation of the corresponding carboxaldehydes.

2. Depending on the structure of the acid chloride, either transamidation or aldehyde formation can occur.

3. A general scheme is proposed for the reactions of acid chlorides with dimethylformamide.

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