NEW REACTION OF TERTIARY AMINES WITH FLUORINATED ACID HALIDES*

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We here report an investigation of the previously unknown reaction of fully halogenated acid halides with triethylamine, as a result of which aminoalkenones of type (III) are formed. Previously, reactions have been carried out between tertiary amines and acid halides without hydrogen atoms in the α-position relative to the haloformyl group for the case of aromatic acid chlorides [2], dialkylcarbamoyl chlorides [2], and phosgene [2-4]. In all these cases there is probably initial formation of quaternary acylammonium halides (I), which are unstable and reactive substances and undergo further transformations:

$$ArCOX + NEt_3 \rightarrow \underset{(I)}{[ArCONEt_3]^+X^-}. \quad (1)$$

As regards the aminoalkenones (III), only one compound of this type is known, namely 4-anilino-1,1,1-trichloro-3-buten-2-one [5], prepared by a multistage synthesis from methyl 1,2,2,2-tetrachloroethyl ether. The usual methods for the preparation of aminoalkenones [6-9] are not applicable for the synthesis of aminohaloalkenones of type (III).

This new reaction was studied in greatest detail for the case of trichloroacetyl chloride [Eq. (2)]. It was found that trichloroacetyl chloride (IIa) reacts with triethylamine under mild conditions and gives good yields of 1,1,1-triethylamine hydrochloride. The other acid halides (IIb)-(IIf) react analogously with triethylamine in accordance with Eq. (2).

$$\underset{(II)}{2RCOX} + 3NEt_3 \rightarrow \underset{(III)}{RCOCH=CHNEt_2} + \underset{(IV)}{RCH=O} + Et_3NH^+X^- \quad (2)$$

$$R = CCl_3(a);\quad CF_3(b);\quad C_3F_7(c);\quad (CF_3)_2CF(d);\quad (CF_3)_2CCl(e);$$
$$(CF_3)_2C(f).\ X = Cl \text{ or } F.$$

To prove the structure of the aminoalkenone (IIIa) this was prepared independently from diethylamine and 1,1,1,4-tetrachloro-3-buten-2-one (V) in accordance with Eq. (4). In its turn, the latter was synthesized in very low yield by the addition of trichloroacetyl chloride to acetylene [Eq. (3)].

$$CCl_3COCl + CH \equiv CH \xrightarrow{AlCl_3} \underset{(V)}{CCl_3COCH=CHCl} \quad (3)$$

$$\underset{(V)}{CCl_3COCH=CHCl} + 2NHEt_2 \rightarrow \underset{(IIIa)}{CCl_3COCH=CHNEt_2} + Et_2NH_2^+Cl^-. \quad (4)$$

The spectral characteristics of the aminoalkenones (III) (an absorption band at 930-970 cm^{-1} in the IR spectrum and the spin–spin interaction constant for unsaturated protons in the PMR spectrum) indicate that these compounds are probably of trans configuration (see [9]).

In the examination of the reaction mechanism it is useful to draw an analogy with a number of processes occurring via the formation of charge–transfer complexes. Such a viewpoint on the mechanism of the reactions of aroyl halides with tertiary amines has already been expressed in [10]. Closely allied to the conversion of acid halides into aminoalkenones which we have discovered is the known reaction between tetrachloro-p-benzoquinone and triethylamine, in which trichloro(diethylaminovinyl)-p-benzoquinone is

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obtained [11]. On analogy to the latter reaction the mechanism of the reaction of a tertiary amine with an acid chloride is as follows (the equation is written for one of the cases investigated by us):

$$CF_3COF + NEt_3 \rightarrow [CF_3COF \leftarrow \underset{(VI)}{Et_3N}] \rightarrow \left[\underset{(VII)}{CF_3\dot{C}F{-}O^-\ \ Et_2\overset{+}{\dot{N}}{-}CHCH_3}\right] \rightarrow$$

$$\left[CF_3CH{-}O^-\ \ Et_2\overset{+}{N}{=}CH{-}CH_2\right] \rightarrow CF_3CH{=}O + HF + \underset{(VIII)}{Et_2NCH{=}CH_2}$$

$$CF_3COF + CH_2{=}CHNEt_2 \xrightarrow{NEt_3} CF_3COCH{=}CHNEt_2.$$

The acid halide and the tertiary amine first form the adduct (VI), in which the transfer of an electron from the donor (amine) to the acceptor (acid halide) is effected. The complex (VII) of the radical cation of triethylamine and the radical anion of the acid halide is then formed. The radical cation of triethylamine is a source of hydrogen, which reduces the acid fluoride to the aldehyde and is itself converted into the extremely unstable N,N-diethylvinylamine (VIII) [12, 13]. The latter is acylated by a second molecule of the acid fluoride with formation of the final reaction product, the aminoalkenone (see the acylation of enamines [14, 15]).

We attempted to prove the intermediate formation of a charge–transfer complex in the reaction between trichloroacetyl chloride and triethylamine by means of the ESR spectrum and the measurement of absorption spectra in the visible region. However, we did not obtain an ESR signal (see [10]), and the determination of the visible spectrum was hindered by the presence of a precipitate of triethylamine hydrochloride. When we used N,N,N',N'-tetramethyl-p-phenylenediamine instead of triethylamine, we were able to obtain absorption bands of the radical cation of N,N,N',N'-tetramethyl-p-phenylenediamine (see [10]), which provides an argument in favor of the intermediate formation of a charge–transfer complex also in the reaction with triethylamine.

The reaction probably goes both with acid chlorides and with acid fluorides, but in one case (heptafluorobutyryl halides) we succeeded in bringing about reaction only with the acid fluoride. In the case of the acid (IIc) we obtained a complex mixture of unidentified products, in which the required aminoalkenone (IIIc) was present only in very small amount. In the reaction of nonafluoropivaloyl fluoride (IIf) with triethylamine, as well as the corresponding aminoalkenone (IIIf) we isolated 2H-hexafluoro-2-(trifluoromethyl)propane (X) which probably arose by the decarbonylation of the corresponding aldehyde (IX) (see [16]).

$$\underset{(IIf)}{(CF_3)_3CCOF} + NEt_3 \rightarrow [\underset{(IX)}{(CF_3)_3CCH{=}O}] + \underset{(IIIf)}{(CF_3)_3CCOCH{=}CHNEt_2} \qquad (5)$$

$$\rightarrow \underset{(X)}{(CF_3)_3CH} + CO.$$

Aldehydes in general, and particularly perfluoroaldehydes, readily polymerize, and it is difficult to isolate them from the reaction mixture. We succeeded in isolating them only in the case of chloral (IVa) and heptafluorobutyraldehyde (IVc).

The most interesting of the acid halides investigated proved to be 2-chloro-3,3,3-trifluoro-2-(trifluoromethyl)propionyl fluoride (IIe), in which triethylamine reduces not only the fluorine atom of the fluoroformyl group, but also the chlorine atom (see the reduction of a halogen atom in aliphatic fluorine compounds [17]). As well as the aminoalkenone (IIIe), in this reaction we found also the known adduct (XI) [18] of 3,3,3-trifluoro-2-(trifluoromethyl)propionyl fluoride with triethylamine.

$$(CF_3)_2CClCOF \xrightarrow{NEt_3} \begin{cases} \rightarrow \underset{(IIIe)}{[(CF_3)_2CClCH{=}O] + (CF_3)_2CClCOCH{=}CHNEt_2} & (6) \\ \rightarrow (CF_3)_2CHCOF \xrightarrow{NEt_3} \underset{(XI)}{(CF_3)_2C{=}CFOH\cdots NEt_3}. & (7) \end{cases}$$

Apart from acid halides, epoxyfluoroalkanes also react with triethylamine [19]; they are first isomerized into acid fluorides [20, 21]. In the present work we investigated this reaction for the case of 1,2-epoxylpentafluoro-2-(trifluoromethyl)propane (XII).

$$\underset{(XII)}{(CF_3)_2C{-}CF_2\ (O)} \xrightarrow{NEt_3} [(CF_3)_2CFCOF] \xrightarrow{NEt_3} (CF_3)_2CFCOCH{=}CHNEt_2. \qquad (8)$$

On the other hand, unhalogenated acid chlorides do not give aminoalkenones, which we specially checked by repeating the known reactions of benzoyl chloride and phosgene with tertiary amines. In the second case we obtained diethylcarbamoyl chloride (XIII) [Eq. (9)]. Similar dealkylation of tertiary amines is known for such pairs as benzoyl chloride and N,N-dimethylbenzylamine [22], phosgene and trimethylamine [2, 3] or N,N-dialkylanilines [4], and acetyl bromide and N,N-dimethylaniline [22].

$$COCl_2 + 2NEt_3 \rightarrow \underset{(XIII)}{ClCONEt_2} + Et_3NH^+Cl^-. \quad (9)$$

Enhanced electrophilic activity of the acid halides is evidently necessary for the success of the reaction under examination, and this exists when a perhaloalkyl group is present. However, the electrophilicity of the aromatic nucleus in benzoyl chloride is not sufficient for the conversion of the latter into the corresponding aminoalkenone.

It was of interest to use not only triethylamine, but also other amines in the reactions with acid halides. It was found that the replacement of triethylamine by trimethylamine in the reaction with trichloroacetyl chloride leads only to the product of the cleavage of the amine – 2,2,2-trichloro-N,N-dimethylacetamide (XIV):

$$CCl_3COCl + 2NMe_3 \rightarrow \underset{(XIV)}{CCl_3CONMe_2} + Me_4N^+Cl^-. \quad (10)$$

In the reaction of trichloroacetyl chloride with N, N-diethylaniline, as well as the expected trichloro(N-ethylanilino)butenone (XV) we obtained the product of the acylation of N,N-diethylaniline in the para position [2,2,2-trichloro-4'-(diethylamino)acetophenone (XVI)] and Ethyl Violet (XVII).

$$CCl_3COCl + Et_2NPh \rightarrow \underset{(XV)}{CCl_3COCH{=}CHNEtPh} \quad (11)$$

$$CCl_3COCl + Et_2NPh \rightarrow \underset{(XVI)}{p\text{-}CCl_3COC_6H_4NEt_2} \quad (12)$$

$$CCl_3COCl + Et_2NPh \rightarrow \underset{(XVII)}{(Et_2NC_6H_4)_3C^+Cl^-}. \quad (13)$$

In the PMR spectrum of the aminoalkenone (XV) a component of the AB quartet of unsaturated protons in the weak field (NCH proton) is a highly broadened doublet, which can probably be explained by the steric proximity of the phenyl nucleus. It should be noted that in the PMR spectra of all the aminoalkenones (III) synthesized the N-ethyl groups are nonequivalent and have different chemical shifts. This phenomenon arises from the fact that the aminoalkenones are vinylogs of tertiary amides. It is known [23] that the latter give similar PMR spectra.

The triphenylmethane dye is formed in the reactions of trichloroacetyl chloride with N,N-diethylaniline and with N,N-dimethylaniline (see below) probably in accordance with a scheme analogous to that described in [24]. As regards the corresponding aminophenones obtained also in other reactions of perhalo acid halides with N,N-dialkylanilines [Eq. (14)], here the ease with which the acylation of the nucleus occurs is noteworthy. This ease is evidently related to the already mentioned enhanced electrophilicity of perfluorinated acid chlorides.

$$RCOCl + PhNR'_2 \rightarrow \underset{(XVIII)}{RCOC_6H_4NR'_2} + HCl \quad (14)$$

$R = CCl_3$ $R' = Me$ (a): $R = C_3F_7$ $R' = Et$ (b)

It is known that N,N-dimethylaniline can be acylated in the para position by phosgene [25] and oxalyl chloride [25], but, nevertheless, the acylation of N,N-dialkylanilines by acid chloride to aminophenones of type (XVIII) is usually effected in presence of aluminum chloride [27], or aminophenones are obtained from amides and N,N-dialkylanilines by the Vilsmeier-Haack reaction [28].

EXPERIMENTAL*

Melting points are uncorrected. PMR spectra were recorded on a Hitachi H-6013 spectrometer in acetonitrile solution for aminoalkenones and in CCl_4 solution for other substances with hexamethyldisiloxane

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as internal standard; spectra are given in the δ scale relative to tetramethylsilane. IR spectra were with KBr in the case of solids and on thin layers in the case of liquids. Visible spectra were recorded on an SF-4M spectrophotometer. GLC analysis was conducted on columns containing liquid Thiokol (Mark 1 from the Kazan' factory), tetramethylene dibutyrate, and polychlorotrifluoroethylene. TLC was conducted on silica (150 mesh) and alumina (deactivated with 5% acetic acid).

1,1,1-Trichloro-4-(diethylamino)-3-buten-2-one (IIIa)

From Trichloroacetyl Chloride (IIa). The acid chloride (IIa) (11.4 g) was added with stirring to a solution of 9.4 g of dry triethylamine in 50 ml of dry benzene at 20°C, and the mixture was left for 12 h. Triethylamine hydrochloride was filtered off (7.7 g), and the benzene solution was extracted with water. The residue remaining when benzene had been driven off was crystallized from petroleum ether. We obtained 5.7 g (78%) of the aminobutenone (IIIa), mp 55-56°C; ν_{max} 1580 cm^{-1} (C = C), 1660 cm^{-1} (C = O). PMR spectrum: 1.20 and 1.25 (two triplets of Me groups on two CH_2 groups, J 7.6 Hz); 3.39 and 3.50 (two corresponding CH_2 quartets); 5.68 and 7.81 (AB quartet of CH = CH, J 13 Hz). Found: C 39.3; H 4.96; N 5.72%. $C_8H_{12}Cl_3NO$. Calculated: C 39.3; H 4.94; N 5.74%. The aqueous extract was washed with benzene and extracted with ether, the ether extracts were dried, ether was driven off, and the residue was distilled from its mixture with concentrated H_2SO_4. We obtained 0.6 g (15%) of chloral (IVa), identical to a known sample (GLC).

From 1,1,1,4-Tetrachloro-3-buten-2-one (V). Acetylene was passed rapidly through a mixture of 40 g of $AlCl_3$, 110 ml of CCl_4, and 42 g of the acid chloride (IIa) for a period of 3 h, first at 20°C, and then at 50°C. The mixture was poured onto ice, the organic layer was separated and dried, solvent was driven off, and by the distillation of the residue we obtained 0.5 ml of a mixture of the chloro ketone (V) and trichloroacetic acid, bp 80-90°C (19 mm). This mixture was washed with aqueous sodium bicarbonate solution, diethylamine was added to the residue at 0°C, the mixture was left for 30 min, and the crystals formed were washed with water, dried, and crystallized from petroleum ether. We obtained 0.1 g of the aminobutenone (IIIa).

Investigation of the Spectra of Mixtures of Trichloroacetyl Chloride (IIa) with Amines

Mixtures of trichloroacetyl chloride (IIa) and triethylamine in molar proportions of 1.1:0.5, 1.2:1.3, and 1.0:1.7 in dry ether and of 1.0:1.5 in acetonitrile were sealed in an atmosphere of nitrogen in ampoules for the determination of ESR spectra at –78°C. No ESR signals were detected in these mixtures in the temperature range from –78 to +20°C with an ÉR-1301 spectrometer. In an atmosphere of nitrogen at 20°C $1 \cdot 10^{-4}$ M acetonitrile solutions of the acid chloride (IIa) and triethylamine were mixed, and there was an immediate voluminous precipitate which made the determination of the visible spectrum difficult. In an atmosphere of nitrogen at 20°C a $1.07 \cdot 10^{-2}$ M acetonitrile solution of the acid chloride (IIa) was mixed with a $1.01 \cdot 10^{-2}$ M acetonitrile solution of N,N,N',N'-tetramethyl-p-phenylenediamine; there was a bluish-violet coloration with a broad absorption band starting at 420 mμ and continuing into the IR region with λ_{max} at 570 and 615 mμ ($\varepsilon = 1.13 \cdot 10^2$ and $1.10 \cdot 10^2$ respectively). According to [10], the radical cation has λ_{max} 565 and 615 mμ.

4-(Diethylamino)-1,1,1-trifluoro-3-buten-2-one (IIIb)

From Trifluoroacetyl Chloride (IIb). A mixture of 35 g of the acid chloride (IIb), 47.3 g of dry triethylamine, and 50 ml of dry benzene was left in a steel autoclave for 12 h at 0°C. The mixture was washed with water and hydrochloric acid and dried, benzene was driven off, and the residue was distilled. We obtained 7.4 g (35%) of the aminobutenone (IIIb), bp 97-98°C (2mm); n_D^{23} 1.4867, mp 12-13°C; ν_{max} 1580 cm^{-1} (C = C) and 1675 cm^{-1} (C = O). PMR spectrum: 1.23 and 1.29 (two triplets of Me group on two CH_2 groups, J 7.3 Hz); 3.32 and 3.47 (two corresponding CH_2 quartets); 5.55 and 7.92 (AB quartet of CH = CH, J 13 Hz). Found: C 48.5; H 6.12; F 30.0; N 7.29%. $C_8H_{12}F_3NO$. Calculated: C 49.2; H 6.20; F 29.2; N 7.27%.

From Trifluoroacetyl Fluoride (IIb). In an analogous way from 12.7 g of the acid fluoride (IIb) in the course of 12 h at 100°C we obtained 2.3 g (21.5%) of the aminobutenone (IIIb).

1-(Diethylamino)-4,4,5,5,6,6,6-heptafluoro-1-hexene-3-one (IIIc)

From Heptafluorobutyryl Fluoride (IIc). A mixture of 19 g of the acid fluoride (IIc) and 13.5 g of dry triethylamine was left at 20°C for 7 days, washed with dilute HCl, $NaHCO_3$ solution, and water, and extracted with ether. The extract was dried, ether was driven off, and we obtained 6 g (45%) of the aminohexanone (IIIc), bp137-138°C (7 mm), freezing at 20°C; ν_{max} 1580 cm^{-1} (C=C) and 1660 cm^{-1} (C=O). PMR spectrum: 1.28 and 1.34 (two triplets of Me groups on two CH_2 groups, J 7.3 Hz); 3.42 and 3.53 (two corresponding CH_2 quartets); 5.40 and 8.05 (AB quartet of CH=CH, J 13 Hz). Found: C 40.0; H 4.00; N 4.75; F 45.5%. $C_{10}H_{12}H_7NO$. Calculated: C 40.7; H 4.07; H 4.06; N 4.77; F 45.1%.

From Heptafluorobutyryl Chloride (IIc). A mixture of 14.6 g of the acid chloride (IIc) and 9.5 g of dry triethylamine in 70 ml of dry ether was left overnight, and 8.3 g of triethylamine hydrochloride was filtered off. Ether and low-boiling substances were driven from the filtrate in a vacuum into a trap at –78°C, and the residue was distilled at 106-122°C (2 mm) and chromatographed on silica with a 2:1 mixture of benzene and chloroform as eluent. We obtained 0.2 g (2%) of the aminohexenone (IIIc).

From a part of the ethereal solution (from the trap) with 2,4-dinitrophenylhydrazine we prepared heptafluorobutyraldehyde 2,4-dinitrophenylhydrazone, mp 106.5-107°C (60% dioxane); [29] gives mp 107°C. Found: N 15.3; F 34.8%. $C_{10}H_5F_7N_4O_4$. Calculated N 14.8; F 35.2%.

1-(Diethylamino)-4,5,5,5-tetrafluoro-4-(trifluoromethyl)-1-penten-3-one (IIId)

From Tetrafluoro-2-(trifluoromethyl)propionyl Fluoride (IId). Analogously to the experiment on the preparation of (IIIb), from 6.7 g of the acid fluoride (IId) and 4.7 g of triethylamine we obtained 1.8 g (41%) of the aminopentenone (IIId), mp 86.5-87°C (heptane); ν_{max} 1585 cm^{-1} (C=C) and 1660 cm^{-1} (C=O). PMR spectrum: 1.25 and 1.30 (two triplets of Me groups on two CH_2 groups, J 7.1 Hz); 3.30 and 3.50 (two corresponding CH_2 quartets); 5.39 and 9.02 (AB quartet of CH=CH, J 13 Hz); the COCH doublet (5.39) is further split into a doublet by the F atom of CF as a result of remote interaction. Found: C 41.10; H 3.95; F 44.4; N 5.10%. $C_{10}H_{12}F_7NO$. Calculated: C 40.7; H 4.07; F 45.2; N 4.75%.

From 1,2-Epoxypentafluoro-2-(trifluoromethyl)propane (XII). In an analogous way from 3.1 g of the epoxide (XII) and 1.45 g of triethylamine we obtained 1.1 g (45%) of the aminopentenone (IIId).

4-Chloro-1-(diethylamino)-5,5,5-trifluoro-4-(trifluoromethyl)-1-penten-3-one (IIIe)

Analogously to the experiment on the preparation of (IIIb), from 5 g of 2-chloro-3,3,3-trifluoro-2-(trifluoromethyl)propionyl fluoride (IIe) and 6.5 g of dry triethylamine we obtained, after the fractionation of the reaction mixture, 2 g of the adduct (XI) of 3,3,3-trifluoro-2-(trifluoromethyl)propionyl fluoride with triethylamine [by the action of methanol and water the adduct (XI) was converted into a mixture of (trifluoromethyl)malonic and methoxypropionic esters [18], identified with known samples by means of GLC was obtained together with a residue, which crystallized on standing. Recrystallization from heptane gave 0.85 g (27%) of the aminopentenone (IIIe), mp 95-95.5°C, ν_{max} 1580 cm^{-1} (C=C) and 1658 cm^{-1} (C=O). PMR spectrum: 1.24 and 1.26 (two triplets of Me groups on two CH_2 groups, J 7.1 Hz); 3.34 and 3.50 (two corresponding CH_2 quartets); 5.62 and 7.95 (AB quartet of CH=CH, J 13 Hz). Found: C 38.7; H 3.87; Cl 11.0; N 3.94%. $C_{10}H_{12}ClF_6NO$. Calculated: C 38.4; H 3.86; Cl 11.3; N 4.49%.

1-(Diethylamino)-5,5,5-trifluoro-4,4-bis(trifluoromethyl)-1-penten-3-one (IIIf)

A mixture of 1.5 g of nonafluoropivaloyl fluoride (IIf) and 0.85 g of dry triethylamine was left in a glass ampoule for 14 days at 20°C (the ampoule was opened from time to time to release liberated CO). Low-boiling substances were distilled under somewhat reduced pressure at 20°C into a trap (–78°C), and the residue was treated with 25 ml of acidified water and crystallized from petroleum ether. We obtained 0.25 g (26%) of the aminopentenone (IIIf), mp 68.5-69°C, ν_{max} 1585 cm^{-1} (C=C) and 1677 cm^{-1} (C=O). PMR spectrum 1.25 and 1.38 (two triplets of Me groups on two CH_2 groups, J 7.3 Hz); 3.37 and 3.58 (two corresponding

CH_2 quartets); 5.18 and 7.07 (AB quartet of CH = CH, J 12 Hz). Found: C 38.4; H 3.27; F 48.7; N 4.38%. $C_{11}H_{12}F_9NO$. Calculated C 38.4; H 3.50; F 49.5; N 4.05%.

The liquid in the trap (0.4 g) was 2H-hexafluoro-2-(trifluoromethyl)propane (X) (yield 60%), identical to a known sample [30] (GLC).

Diethylcarbamoyl Chloride (XIII)

A mixture of 15 g of phosgene and 45 g of dry triethylamine in 14 ml of dry ether was left in a glass ampoule for 2 days at 20°C. Triethylamine hydrochloride was filtered off (7 g), solvent was driven off, and the residue was vacuum-distilled twice. We obtained 15 g (74%) of diethylcarbamoyl chloride (XIII), bp 51-52°C (3 mm); [31] gives bp 190-195°C. Found: C 43.9; H 7.44%. $C_5H_{10}ClNO$. Calculated: C 44.2; H 7.43%.

Reaction of Benzoyl Chloride with Triethylamine

A mixture of 14 g of benzoyl chloride and 20.2 g of dry triethylamine was heated for 15 h at 98°C and then vacuum-distilled. We obtained 9 g of unchanged benzoyl chloride and a nondistilling residue, in which by means of TLC we could not detect 3-(diethylamino)acrylophenone.*

2,2,2-Trichloro-N,N-dimethylacetamide (XIV)

A mixture of 30 g of trichloroacetyl chloride (IIa), 20 g of dry trimethylamine, and 30 ml of dry benzene was heated for 15 h at 50°C. The mixture was filtered, washed with water, dried, and vacuum-distilled. We obtained 9 g (29%) of the amide (XIV), bp 92-93°C (8 mm) [[32] gives bp 84°C (4 mm)], identical according to GLC and the IR spectrum to the substance obtained from the acid chloride (IIa) and dimethylamine.

1,1,1-Trichloro-4-(N-ethylanilino)-3-buten-2-one (XV)

A mixture of 9.5 g of dry N,N-diethylaniline and 7.76 g of trichloroacetyl chloride (IIa) was left in the dark for 2 days at 20°C. The mixture was treated with 100 ml of water and extracted first with benzene, and then with chloroform. The benzene solution was washed several times with concentrated HCl. The benzene solution was then dried, benzene was vacuum-distilled off, and we obtained 0.8 g (6.5%) of the trichloro(N-ethylanilino)butenone (XV), mp 71-72°C (petroleum ether), ν_{max} 1570-1575 cm^{-1} (C = C) and 1660 cm^{-1} (C = O). PMR spectrum: 1.2 (triplet of Me on CH_2 group, J 8.2 Hz); 3.78 (corresponding CH_2 quartet); 5.85 (broad) and 7.3 (AB quartet of CH = CH, J 14 Hz); 6.6 (multiplet of Ph). Found: C 49.8; H 4.23; N 4.92%. $C_{12}H_{12}Cl_3NO$. Calculated C 49.6; H 4.16; N 4.82%. On dilution of the hydrochloric acid solution with water we obtained 6.5 g (53%) of 2,2,2-trichloro-4'-(diethylamino)acetophenone (XVI), mp 105.5-106°C (petroleum ether), ν_{max} 1460, 1480, 1544, and 1600 cm^{-1} (Ph); 1678 cm^{-1} (C = O). PMR spectrum: 1.22 (triplet of Me on CH_2, J 8.2 Hz); 3.52 (corresponding CH_2 quartet); 6.5 and 8.0 quartet of Ph, J 10 Hz). Found: C 48.7; H 4.88; N 4.86%. $C_{12}H_{14}Cl_3NO$. Calculated: C 48.9; H 4.78; N 4.75%.

With concentrated HCl the aminophenone (XVI) gave a colorless hydrochloride, which decomposed into the original compounds when heated or dissolved in water. From the chloroform solution by chromatography on alumina with a 2% solution of methanol in chloroform as eluent we obtained 0.01 g of Ethyl Violet (XVII) λ_{max} 595 mμ ($\varepsilon = 0.94 \cdot 10^5$) in 95% alcohol; according to [33], $\varepsilon = 10^5$ at 595 mμ.

2,2,2-Trichloro-4'-(dimethylamino)acetophenone (XVIIIa)

A mixture of 5.78 g of dry N,N-dimethylaniline and 5.8 g of trichloroacetyl chloride (IIa) was left in the dark for 2 days at 20°C. The dark-blue crystalline mass was treated with water and extracted, first with ether and then with chloroform. From the ethereal solution we obtained 4.9 g (58%) of the aminophenone (XVIIIa), mp 86-87°C (petroleum ether); ν_{max} 1455, 1495, 1540, and 1600 cm^{-1} (Ph); 1690 cm^{-1} (C = O). PMR spectrum: 3.04 (Me); 6.5 and 8.0 (A_2B_2 quartet of Ph, J 10 Hz). Found: C 44.7; H 3.79; Cl 40.0%. $C_{10}H_{10}Cl_3NO$. Calculated 45.1; H 3.77; Cl 39.9%. From the chloroform solution by chromatography on alumina we obtained 0.01 g of Crystal Violet, λ_{max} 591 mμ in 95% alcohol; [34] gives λ_{max} 590 mμ.

* A sample of 3-(diethylamino)acrylophenone was kindly provided by M. I. Rybinskaya.

4'-(Diethylamino)-2, 2, 2, 3, 4, 4, 4-hexafluorobutyrophenone (XVIIIb)

A mixture of 5.66 g of dry N,N-diethylaniline and 5.88 g of heptafluorobutyryl chloride (IIc) was left in the dark for 2 days at 20°C. The violet crystalline mass was treated with water and extracted with benzene. The benzene solution was washed with acidified water, dried, and chromatographed on alumina with benzene as eluent. We obtained 5.5 g (63%) of the aminophenone (XVIIIb), mp 27-28°C (80% methanol); ν_{max} 1455, 1480, 1550, and 1604 cm^{-1} (Ph); 1680 cm^{-1} (C = O). PMR spectrum: 1.22 (triplet of Me on CH_2, J 8.2 Hz), 3.52 (corresponding CH_2 quartet); 6.54 and 7.85 (A_2B_2 quartet of Ph, J 9 Hz). Found: C 48.8; H 4.46; F 38.6%. $C_{14}H_{14}F_7NO$. Calculated: C 48.7; H 4.08; F 38.5%.

CONCLUSIONS

A detailed study was made of the new reaction of perhaloacyl halides with triethylamine, which leads to the formation of (diethylamino)alkenones.

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