FLUORO-CONTAINING HETEROCUMULENES

COMMUNICATION 10.* N-PHENYLTRIFLUOROMETHYLCARBALKOXYKETENIMINES

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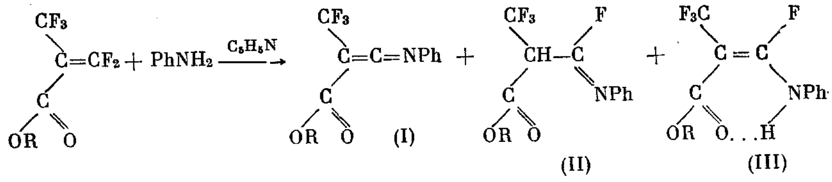
A method was developed previously for the synthesis of bis(trifluoromethyl)ketenimines with various substituents attached to the nitrogen atom and some of their properties were studied [2, 3]. It seemed of interest to ascertain how the reactivity is affected by replacing one CF_3 group in bis(trifluoromethyl)ketenimine by a higher electron–acceptor ester grouping. The (I) ketenimines were synthesized by us by reacting the esters of perfluoromethacrylic acid with aniline. The same as in the reaction of primary amines with perfluoroisobutylene [2], in this case the composition of the reaction products depends on the ratio of the reactants and the nature of the tertiary amine that is used as the catalyst. The (I) ketenimines were obtained in up to 70% yield when Et_3N was used, while the use of pyridine gives a mixture of ketenimines (I), imidoyl fluorides (II), and their isomeric enamines (III). The pure (I) ketenimines can be obtained by treating this mixture with powdered KOH in ether



R = CH_3 (a), C_2H_5 (b),

It should be mentioned that the formation of the enamine is not observed when perfluoroisobutylene is reacted with primary amines. The comparative stability of the enamine (III) is evidently due to the presence of a hydrogen bond between the NH and COOR groups. This is confirmed by the data on the relative amount of imidoyl fluorides (II) and enamines (III) in various solvents, which data were obtained by ^{19}F NMR spectroscopy. As can be seen from Table 1, the enamine : imidoyl fluoride ratio increases with decrease in the ability of the solvent to form the hydrogen bond (DN_{SbCl_5}) [4], while a correlation between the polarity of the solvent [5] and this ratio is not observed.

As was to be expected, the (I) ketenimines are more active in the reactions with nucleophilic reagents than the bis(trifluoromethyl)ketenimines. Thus, ketenimine (I) reacts with tert-butanol in one day, whereas bis(trifluoromethyl)ketenimine does not react completely in 6 months [6]. The higher activity of the (I) ketenimines was also confirmed by the competing reaction of equimolar amounts of bis(trifluoromethyl)ketenimine and the (I) ketenimine with 1 mole of ethanol, where only the (I) ketenimine reacts.

Employing ^{19}F NMR spectroscopy, the formation of the amino acetal (IV) could be observed when (I) is reacted with alcohols, which acetal rearranges quite slowly to the imino ester (V), in which connection this rearrangement is irreversible, in contrast to the analogous transformation of enamine (III) to imidoyl fluoride (II) (cf. [7])

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*See [1] for Communication 9.

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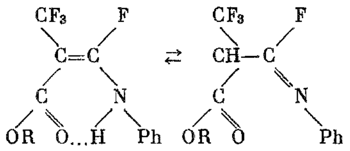
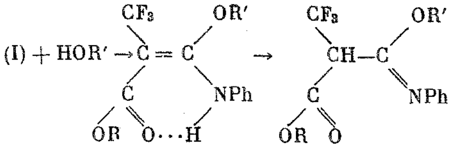
TABLE 1



Solvents*	DN_{SbCl_5}	Relative amount of enamine:imidoyl fluoride	
		$R = C_2H_5$	$R = CH_3$
Hexamethanol	38,8	1 : 3	
Tetramethylurea			1 : 2,5
DMF	26,6	1 : 2,4	
Diethyl ether	19,2	1 : 1,84	
Acetone	17,0	1 : 1,82	
CH_3CN	14,1	1 : 1,78	1 : 1,35
Benzonitrile	11,9	1 : 1,2	
Nitrobenzene	4,4	1,28 : 1	
CCl_4			1,6 : 1

*Equal volumes of solvent and studied compound were used.



(IVa, b, c) (Va, b, c)

$R = R' = C_2H_5$ (IVa); $R = CH_3, R' = CH_2—CH = CH_2$ (IVb);

$R = CH_3, R' = (CH_3)_3C$ (IVc)

The fact that the amino acetal (IV) is formed when the ketenimines are reacted with alcohols is of interest, since it permits assuming that the addition of nucleophiles to heterocumulenes can be accomplished via the C=N bond. It could be reasoned that the intermediate formation of the amino acetal also occurs when the bis(trifluoromethyl)ketenimines are reacted with alcohols. However, in this case the amino acetal, which is not stabilized by hydrogen bonding, would immediately rearrange to the imino ester.

EXPERIMENTAL METHOD

The IR spectra were taken on a UR-20 instrument. The ^{19}F NMR spectra were recorded on a Hitachi instrument (56.46 MHz). The NMR spectra were recorded on a Perkin–Elmer R-12 instrument. The chemical shifts are given in ppm from CF_3COOH (external standard) and HMDS (internal standard).

Reaction of Ethyl Perfluoromethacrylate with Aniline in the Presence of Pyridine. With stirring, to 7.7 g of ethyl perfluoromethacrylate in 10 ml of absolute ether, which contained several drops of pyridine, was added at −78°C a solution of 1.5 ml of aniline in 5 ml of absolute ether. The temperature of the mixture was brought up to ~20° and, after removing the volatile products, the residue was distilled using a high vacuum. We obtained 3.6 g of mixture A, which contained ~11% of ketenimine (Ib), ~48% of imidoyl fluoride (IIb), and ~41% of enamine (IIIb), with bp 83-86° ($\sim 2 \cdot 10^{-3}$ mm). ^{19}F NMR spectrum: (Ib) −22.3 s ($CF_3C=$), (IIb) −13.1 t (CF_3–CH), J_{F-H} = ~10 Hz, −51.5 m (CF), (IIIb) −25.7 d ($CF_3C=$), J_{F-F} = 35.6 Hz, 0.9 d.g. (CF), J_{F-F} = 35.6 Hz, J_{F-H} = ~26 Hz.

N-Phenyltrifluoromethylcarbethoxyketenimine (Ib). With stirring and cooling in ice water, to a suspension of 2.6 g of KOH in 40 ml of absolute ether was added in drops 2.6 g of mixture A in 10 ml of absolute ether at such a rate that the temperature did not exceed 3-5°. The reaction mixture was stirred at this temperature for another 3 h, and then the precipitate was filtered. The filtrate was vacuum-distilled. We obtained 1.9 g (73%) of ketenimine (Ib) with bp 75-76° ($\sim 1 \cdot 10^{-3}$ mm). Infrared spectrum (ν, cm^{-1}): 2080 (C=C=N), 1735 (C=O). NMR spectrum (external standard HMDS): 0.8 t (CH_3), 3.85 g (CH_2), 6.9 s (C_6H_5). Found: C 55.87; H 3.57; F 22.45%. $C_{12}H_{10}F_3NO_2$. Calculated: C 56.00; H 3.89; F 22.14%.

N-Phenyltrifluoromethylcarbomethoxyketenimine (Ia). a) With stirring, to 0.19 mole of methyl perfluoromethacrylate in 10 ml of absolute ether, which contained several drops of Et_3N, was added at −78° a solution of 0.06 mole of aniline in 5 ml of absolute ether. The temperature of the mixture was brought up to ~20°, and the volatile products were vacuum-distilled. The residue was distilled using a high vacuum. We obtained 1 g (65%) of ketenimine (Ia) with bp 76-77° ($\sim 2 \cdot 10^{-3}$ mm). Infrared spectrum (ν, cm^{-1}): 2080 (C=C=N), 1730 (C=O). ^{19}F NMR spectrum: −22.7 s ($CF_3C=$). NMR spectrum (δ, ppm): 3.7 s (CH_3), 7.4 s (C_6H_5). Found: C 53.91; H 3.24; F 23.30; N 5.69%. $C_{11}H_8F_3NO_2$. Calculated: C 54.32; H 3.29; F 23.45; N 5.75%.

b) To 29.6 g of methyl perfluoromethacrylate in 40 ml of absolute ether, which contained several drops of pyridine, was added 4.5 ml of aniline in 15 ml of absolute ether (similar to the experiment with ethyl perfluoromethacrylate). Distillation using a high vacuum gave 9.6 g of mixture B,* which contained ~58% of ketenimine (Ia), ~24% of imidoyl fluoride (IIa), and ~18% of enamine (IIIa), with bp 78-80° ($\sim 2 \cdot 10^{-3}$ mm). The treatment of mixture B with powdered KOH in ether, followed by distillation in a high vacuum, gave 7.2 g (62%) of ketenimine (Ia), which was identical with that described above.

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*The composition of mixture B in % was determined in CH_3CN solution.

Reaction of Ketenimine (Ib) with Ethyl Alcohol. To 0.8 g of ketenimine (Ib) at −78° was added 2 ml of absolute ethyl alcohol, and the temperature was brought up to ~20°. ^{19}F NMR spectrum: (IVa) −25.4 s ($CF_3C=$) ~75%, (Ib) −21.4 s ($CF_3C=$) ~10%, (Va) −13.4 d (CF_3CH) ~15%; after 60 min only −13.4 d (CF_3CH), J_{F-H} = 8 Hz. Subsequent distillation gave 0.6 g (64%) of imino ester (Va) with bp 93-95° ($\sim 4 \cdot 10^{-3}$ mm). Found: C 54.83; H 5.17; F 18.81%. $C_{14}H_{16}F_3NO_3$. Calculated: C 55.44; H 5.27; F 18.81%.

To a mixture of 0.05 g of bis(trifluoromethyl)ketenimine and 0.05 g of ketenimine (Ib) was added 0.009 g of absolute ethyl alcohol in 0.5 ml of absolute ether. ^{19}F NMR spectrum: after 10 min (IVa) −25.4 s ($CF_3C=$), −22.0 s ($(CF_3)_2C=$), (Ib) −21.2 s ($CF_3C=$); after 60 min −22.0 s ($(CF_3)_2C=$), (Va) −13.4 d (CF_3CH).

Reaction of Ketenimine (Ia) with Allyl Alcohol. To 4.5 g of ketenimine (Ia) was added 1.3 g of allyl alcohol. ^{19}F NMR spectrum: after 10 min (IVb) −26.0 s ($CF_3C=$) ~16%, (Ia) −21.6 s ($CF_3C=$) ~44%; (Vb) −13.4 d (CF_3CH) ~40%; after 20 min −26.0 s ($CF_3C=$) ~10%; −21.6 s ($CF_3C=$) ~30%, −13.4 d (CF_3CH) ~60%; after 40 min only −13.4 d (CF_3CH), J_{F-H} = 8 Hz. Vacuum-distillation gave 4.1 g (74%) of imino ester (Vb) with bp 46-48° ($\sim 4 \cdot 10^{-3}$ mm). Found: C 55.79; H 4.80; F 18.88%. $C_{14}H_{14}F_3NO_3$. Calculated: C 55.81; H 4.65; F 18.93%.

Reaction of Ketenimine (Ia) with Tert-Butyl Alcohol. To 1.5 g of ketenimine (Ia) was added 1 g of tert-butyl alcohol. ^{19}F NMR spectrum: after 10 min (IVc) −27.7 s (CF_3C) ~5%, (Ia) −21.4 s ($CF_3C=$) ~95%; after 40 min −27.7 s ($CF_3C=$) ~10%, −21.4 s ($CF_3C=$) ~90%; after 180 min −21.4 s ($CF_3C=$) ~75%, (Vc) −13.1 d (CF_3CH) ~25%. The next day only −13.1 d (CF_3CH), J_{F-H} = 9.7 Hz. We obtained 1.3 g (60%) of imino ester (Vc) with mp 144-146° (from hexane). Found: C 56.41; H 5.74; F 18.03%. $C_{15}H_{18}F_3NO_3$. Calculated: C 56.15; H 5.61; F 17.94%.

CONCLUSIONS

1. Some N-phenyltrifluoromethylcarbalkoxyketenimines were synthesized.

2. The relative stability of the adducts of N-phenyltrifluoromethylcarbalkoxyketenimines at the C=N bond with alcohols and hydrogen fluoride is caused by the presence of an intramolecular hydrogen bond.

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