FLUORINE-CONTAINING IMINES. COMMUNICATION 6.*

REACTION OF HEXAFLUOROACETONE PERFLUOROPIVALOYLIMINE WITH DIMETHYLANILINE AND DIMETHYLBENZYLAMINE

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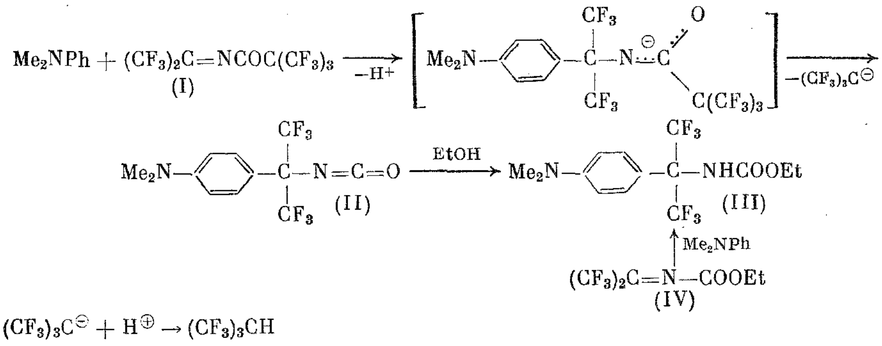
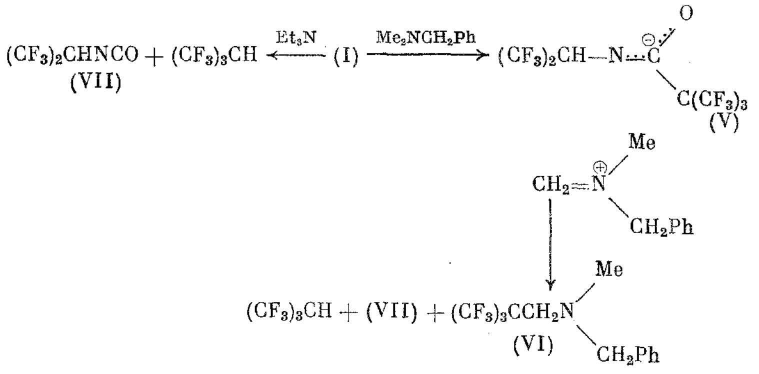
It was determined previously that polyfluoroketone sulfonylimines and hexafluoroacetone trifluoroacetylimine alkylate dimethylaniline and indole [2]. It was found that hexafluoroacetone perfluoropivaloylimine (I) also alkylates dimethylaniline, but that the reaction is accompanied by abstraction of the perfluoro-tert-butyl anion, an efficient leaving group (cf. [3]). As a result of the reaction, isocyanate (II) and monohydroperfluoroisobutane are formed:



The structure of isocyanate (II) was confirmed by spectral data and by identification of urethane (III) obtained from it with the product of back synthesis from carbethoxyimine (IV).

It was determined previously that hexafluoroacetone benzoylimine abstracts a hydride ion from Me_2NCH_2Ph and Et_3N with the formation of immonium salts, whose cations are subsequently deprotonated to methylbenzylaminomethylene and vinyldiethylamine [4]. It was found that in the case of pivaloylimine (I) immonium salt (V)† is also formed, whose cation, however, is not deprotonated, but reacts with the perfluoro-tert-butyl anion that is abstracted from (V) with the formation of amine (VI). In this case, the anion of salt (V) is converted to monohydroisocyanate (VII). In the reaction of (I) with Et_3N, (VII) and monohydroperfluoroisobutane are also obtained.



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*See [1] for Communication 5.
†The salt is unstable and was identified by ^{19}F NMR.

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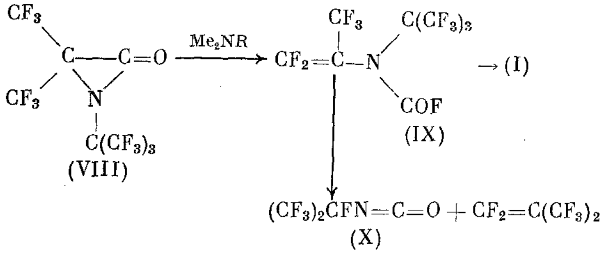
Like (I), the isomer of (I), perfluoro-α-lactam (VIII), reacts with tertiary amines. With dimethylaniline it forms isocyanate (II), and with dimethylbenzylamine it forms monohydroisocyanate (VII) and amine (VI). In addition, carbamoyl fluoride (IX) and its decomposition products perfluoroisopropyl isocyanate (X) and perfluorobutylene are obtained (cf. [5]):



Apparently, with prolonged holding of (VIII) with amines, the initially formed isomer (IX) not only decomposes, but also isomerizes to pivaloylimine (I), which then gives (II), (VI), and (VII) with the amines.

Thus, the presence of the facilely leaving perfluoro-tert-butyl group in acylimine (I) causes the heterodiene (acylimine) to be converted to heterocumulenes (isocyanates).

EXPERIMENTAL

The ^{19}F and ^{1}H NMR spectra (δ, ppm) were recorded on a Perkin-Elmer R-32 spectrometer (^{1}H, 90 MHz; ^{19}F, 84.6 MHz) from CF_3COOH and TMS external standards; the IR spectra were recorded on a UR-20 spectrometer.

α-[p-(Dimethylamino)phenyl]hexafluoroisopropyl Isocyanate (II). To a mixture of 1.5 g of pivaloylimine (I) and 0.45 g of Me_2NPh was added 1.5 ml of abs. ether, and the whole was left for 5 days at 20°C. After monohydroperfluoroisobutane and the ether were driven off, we obtained 0.75 g (66%) of isocyanate (II) with bp 83-84°C (2 mm). Found: C 45.69; H 2.92; F 36.6; N 9.11%. $C_{12}H_{10}F_6N_2O$. Calculated: C 46.2; H 3.2; F 36.5; N 8.89%. IR spectrum (ν, cm^{-1}): 2270 (N=C=O). Proton NMR spectrum: 2.2 broadened singlet (CH_3), 5.7-7.3 multiplet (C_6H_4). Fluorine-19 NMR spectrum: −3.7 singlet (CF_3).

The reaction of (II) with EtOH gave urethane (III), identical to that obtained from carbethoxyimine (IV) and Me_2NPh (^{19}F NMR: −8.1 singlet).

Isocyanates (II) and (X), carbamoyl fluoride (IX), $(CF_3)_3CH$, and $CF_2=C(CF_3)_2$ were formed in the reaction of excess perfluoro-α-lactam (VIII) with Me_2NPh for 2 months (according to ^{19}F NMR).

Reaction of (I) with Me_2NCH_2Ph. To 1.3 g of (I) was added 0.56 g of Me_2NCH_2Ph with cooling. After 5 min, the ^{19}F NMR spectrum of the mixture contained signals at −6.9 and −16.0 ppm (intensity ratio of 2:3) corresponding to salt (V). After 1 h, 0.43 g (71%) of isocyanate (VII), identical to that obtained in [6], was driven off in vacuo (1 mm) into an absorption column (−78°C). Proton NMR spectrum: 4.1 g (CH). Fluorine-19 NMR spectrum: −2.2 doublet (CF_3), J_{F-H} = 5.7 Hz. By distillation of the residue we obtained 0.7 g (87%) of amine (VI) with bp 55-56°C (1 mm). Found: C 44.38; H 3.43%. $C_{13}H_{12}F_9N$. Calculated: C 44.19; H 3.39%. Proton NMR spectrum: 1.9 singlet (CH_3), 3.1 singlet (CH_2), 3.3 singlet (CH_2), 7 singlet (Ph). Fluorine-19 NMR spectrum: −12.2 singlet $(CF_3)_3C$.

Isocyanates (II) and (X), carbamoyl fluoride (IX), $CF_2=C(CF_3)_2$, and $(CF_3)_3CH$ were formed in the reaction of (VIII) with an equimolar amount of Me_2NCH_2Ph in ether after 5 h at 20°C (according to ^{19}F NMR).

The formation of (VII) and $(CF_3)_3CH$ was detected according to the ^{19}F NMR spectrum in the reaction of (I) with an equimolar amount of Et_3N after 0.5 h.

CONCLUSIONS

Hexafluoroacetone perfluoropivaloylimine reacts with dimethylaniline as a C-alkylating agent and with dimethylbenzylimine and triethylamine as a hydride-ion acceptor: the reactions are accompanied by the ejection of perfluoro-tert-butyl anions, which leads to the formation of isocyanates.

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REACTION OF POLYFLUORINATED β-KETOACID ESTERS AND THEIR α-HALO DERIVATIVES WITH PHOSPHORUS PENTACHLORIDE

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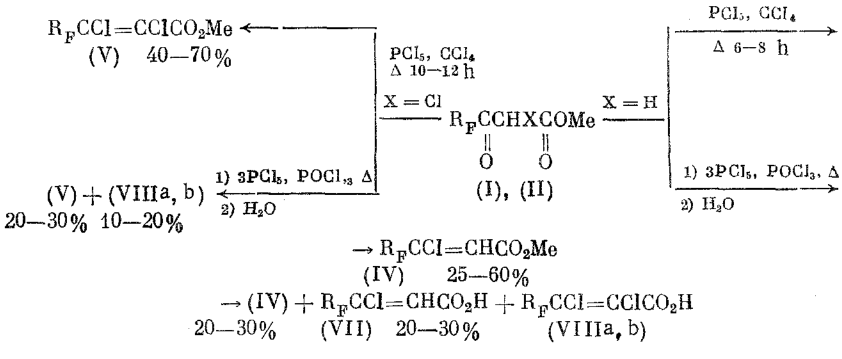
Acetoacetic esters react with PCl_5 in benzene via the carbonyl as well as the ester group (6 h at 0°C and subsequent treatment with water) to give β-chlorocrotonic acid [1, 2]. When the reaction time is decreased to 2 h and the reaction is carried out in $CHCl_3$, a mixture (1:1) of ethyl-β-chlorocrotonate and ethyldichlorobutanoate is also isolated [3]. In this reaction methyl-α-chloroacetoacetate in $CHCl_3$, after treatment with methanol, affords the α,β-dichlorocrotonic ester [4].

However, no information is available about the reaction of PCl_5 with β-ketoesters.

In the present work we studied the reaction of fluoroalkyl- (I), α-chloro- (II), and α,α-dibromo-β-ketoesters (III) with PCl_5 in C_6H_6, $CHCl_3$, CCl_4, and $POCl_3$.

It was shown that compounds (I) and (II), when boiled for 6-12 h with PCl_5 in C_6H_6, $CHCl_3$, and CCl_4, react via carbonyl group R_FCO to form fluorine-containing β-chloro- and α,β-dichlorocrotonic esters (IV) and (V), respectively (as an isomeric mixture; see Table 1). Increasing the reaction time and using excess PCl_5 have no effect on the product composition.



$R_F = HCF_2$ (a), CF_3 (b), C_4F_9 (c), $H(CF_2)_2$ (d).

Using compound (VI), we showed that β-chlorocrotonic esters (IV) of the same isomeric composition are obtained in satisfactory yield when PCl_5 reacts with fluorine-containing β-ketoester copper chelates:

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