REACTION OF PERFLUORO-2-AZAPROPENE WITH ORGANOMAGNESIUM COMPOUNDS

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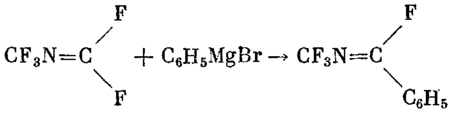
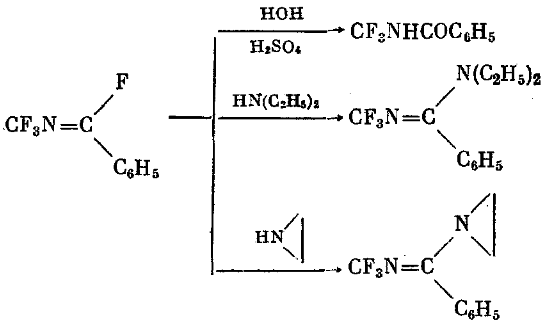
The reaction of perfluoro-2-azapropene (I), which is characterized by a high electrophilicity [1, 2], with organomagnesium compounds was studied in the present paper.

As it proved, (I) reacts easily with Grignard reagents. In contrast to perfluoroisobutylene, which forms the substitution products of vinylic and allylic fluorine atoms [3], the reaction product of (I) with phenylmagnesium bromide is the vinyl derivative 1-phenylperfluoro-2-azapropene (II).


(I) (II)

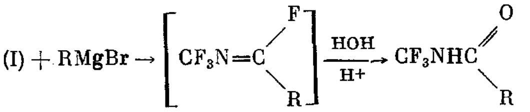
The hydrolysis of (II) with conc. H_2SO_4 leads to the trifluoromethylamide of benzoic acid (III), while diethylamine and ethylenimine react with (II) to give the substitution products of the vinylic fluorine atom.


(III)

(IV)

(V)

The reaction of (I) with alkylmagnesium halides failed to give 1-alkylperfluoro-2-azapropenes, and instead their hydrolysis products, the trifluoromethylamides of the corresponding carboxylic acids, were isolated.


(VI a,b)

$R = C_3H_7$ (a); C_4H_9 (b)

When compared with 1-phenylperfluoro-2-azapropene, the increased sensitivity of the 1-alkylperfluoro-2-azapropenes to acid hydrolysis is explained by the greater "lability" of the vinylic fluorine atom, which is caused by the positive induction effect of the alkyl group.

EXPERIMENTAL

The IR spectra were taken on a Perkin—Elmer-225 instrument (as a thin layer), the ^{19}F NMR spectra were taken on a Perkin—Elmer R-20 instrument (56.46 MHz, standard = CF_3COOH), and the mass spectra were taken on a Varian MAT CH-8 instrument.

1-Phenylperfluoro-2-azapropene (II). To a stirred solution of 15 g of (I) in 60 ml of abs. ether at —70°C was added 100 ml of an ether solution of phenylmagnesium bromide, pre-

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pared from 9.6 g of Mg and 31.4 g of bromobenzene, after which the mixture was warmed up to ∿20°C and then poured on HCl-acidified ice. The ether layer was separated, while the aqueous layer was extracted twice with ether. The combined extract was dried over $MgSO_4$ and distilled to give 19.1 g (50%) of (II), bp 51° (11 mm), n_D^{20} 1.4511. Found: C 48.85; H 2.57; N 6.87. $C_8H_5F_4N$. Calculated: C 50.2; H 2.62; N 7.31%. ^{19}F NMR spectrum (δ, ppm): −23.2 d (CF_3); −48.7 q (CF).

Trifluoromethylbenzamide (III). To 4 g of (II) were added 5 ml of water and 5 ml of conc. H_2SO_4, and the mixture was let stand overnight. The obtained precipitate was separated and recrystallized from benzene to give 3.9 g (97.5%) of (III), mp 103-104°. Found: C 50.38; H 3.18; N 6.94%. $C_8H_6F_3N$. Calculated: C 50.7; H 3.1; N 7.4%.

N,N-Diethyl-N'-trifluoromethylbenzamidine (IV). To a stirred solution of 3.82 g of Et_2NH in 30 ml of abs. ether at −30°C was added a solution of 5 g of (II) in 10 ml of abs. ether, after which the mixture was warmed up to ∿20°, the precipitate was filtered, and the filtrate was vacuum-distilled to give 5.25 g (82%) of (IV), bp 115° (1 mm), n_D^{20} 1.4880. Found: N 10.89%. $C_{12}H_{15}H_2F_3$. Calculated: N 11.46%. ^{19}F NMR spectrum (δ, ppm): −35.5 s (CH_3). Mass spectrum M^+ (m/e): 244 M^+ 172 ($C_8H_5NF_3$), 72 ($C_4H_{10}N$).

N,N-Dimethyleno-N'-trifluoromethylbenzamidine (V). To a stirred mixture of 5 g of (II) and 2.67 g of Et_3N in 15 ml of abs. ether at −40° was added 1.12 g of ethylenimine, after which the cooling was removed, the precipitate was filtered, and the filtrate was vacuum-distilled to give 4.77 g (85%) of (V), bp 107-108° (2 mm), n_D^{20} 1.5144. Found: C 56.14%. $C_{10}H_9N_2F_3$. Calculated: C 56.1%. ^{19}F NMR spectrum (δ, ppm): −35.46 s (CF_3). Mass-spectrum (m/e): 214 (M^+, $C_{10}H_9N_2F_3$), 172 ($C_8H_5NF_3$), 42 (C_2H_4N).

Trifluoromethylamide of Valeric Acid (VIIa). To a stirred solution of 15 g of (I) in 30 ml of abs. ether at −70° was added 60 ml of an ether solution of n-butylmagnesium bromide, prepared from 4 g of Mg and 13.7 g of n-butyl bromide, after which the mixture was warmed up to 20° and poured on HCl-acidified ice. The ether layer was separated, while the aqueous layer was extracted twice with ether, and the combined extract was dried over $MgSO_4$. Vacuum-distillation gave 12.5 g (78%) of (VIIa), bp 107-109° (22 mm). Found: C 42.48; H 6.20; N 8.04%. $C_6H_{10}NOF_3$. Calculated: C 42.05; H 5.92; N 8.27. ^{19}F NMR spectrum (δ, ppm): −20.8 s (CF_3). Infrared spectrum (ν, cm^{-1}): 3280 (NH), 1770 and 1540 (C=O).

Trifluoromethylamide of Butyric Acid (VIIb). Obtained in a similar manner in 80% yield, bp 86-88° (8 mm), mp 36°. ^{19}F NMR spectrum (δ, ppm): −22.2 s (CF_3). Infrared spectrum (ν, cm^{-1}): 3300 (NH), 1700 (C=O). Mass spectrum: 112 (C_2HNF_3O), 43 (C_3H_7).

CONCLUSIONS

1. Perfluoro-2-azapropene reacts with phenylmagnesium bromide to give the vinylic substitution product, namely 1-phenylperfluoro-2-azapropene.

2. The reaction of perfluoro-2-azapropene with alkylmagnesium halides led to the isolation of the hydrolysis products of the 1-alkylperfluoro-2-azapropenes, namely the trifluoromethylamides of the corresponding carboxylic acids.

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