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THE REACTIONS OF POLYFLUOROCARBONYL COMPOUNDS WITH PHENYLHYDRAZINES

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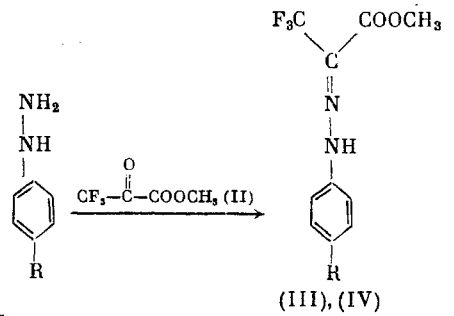
Methyl trifluoropyruvate (II) reacts with phenylhydrazine and *p*-nitrophenylhydrazine to give the corresponding phenylhydrazones (III) and (IV). The reaction of phenylhydrazine with hexafluoroacetone (I) at 20°C leads to the product of the C^2-hydroxyalkylation of the aromatic ring (V). The hydroxyalkylation of hydrazobenzene under the same conditions is complicated by a benzidine rearrangement.

The reaction of hexafluoroacetone (I) and methyl trifluoropyruvate (II) with arylamines leads to stable C-hydroxyalkylation products [1-8]. In the case of ketoester (II), ortho substitution in the aromatic ring, as a rule, is accompanied by lactamization. Furthermore, ketoester (II), in contrast to ketone (I), is capable of forming Schiff bases with arylamines [1, 9]. In the present work, we studied the reactions of polyfluorocarbonyl compounds (I) and (II) with arylhydrazines.

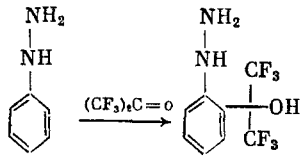
The reaction of phenylhydrazine with ketoester (II) in $CHCl_3$ at 80°C gives the quantitative formation of phenylhydrazone (III). Hydrazone (IV) was obtained under similar conditions from *p*-nitrophenylhydrazine and ketoester (II).



(III), (IV)

R = H (III), NO_2 (IV).

Ketone (I) alkylates phenylhydrazine even at 20°C to give the exclusive formation of the product of C^2-substitution in the aromatic ring (V).



(V)

The change from the para orientation of the C-hydroxyalkylation by ketone (I) characteristic for anilines [1, 2] is apparently a consequence of a cyclic transition state arising as a result of the equilibrium N-hydroxyalkylation reaction of the primary amino group [1]. *p*-Nitrophenylhydrazine does not form stable reaction products with ketone (I) even at 100°C.

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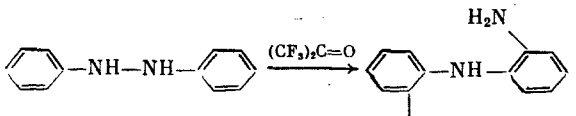
TABLE 1. Characteristics of (III)-(VI)

Compound	Yield, %	R_f (eluent)	Mp, °C	Found / Calc. C	Found / Calc. H	Found / Calc. N	Chemical formula	M^+
(III)	98	0.9 (C)	42–43	48,51 / 48,78	3,47 / 3,65	11,02 / 11,38	$C_{10}H_9F_3N_2O_2$	246
(IV)	93	0.5 (C)	174–175	41,05 / 41,23	2,80 / 2,75	14,25 / 14,40	$C_{10}H_8F_3N_3O_4$	291
(V)	77	0.5 (B)	125–127	39,25 / 39,41	2,71 / 2,91	10,01 / 10,21	$C_9H_8F_6N_2O$	274
(VI)	25	0,38 (A)	145–146	51,39 / 51,42	3,12 / 3,42	7,94 / 8,00	$C_{15}H_{12}F_6N_2O$	

The treatment of hydrazobenzene by ketone (I) at 20°C also leads to a complex mixture of substituted products of the benzidine rearrangement, which yielded *o*-semidine derivative (VI).



(VI)

The structures of (III)-(VI) were established by elemental analysis (Table 1), ^1H, ^{19}F, and ^{13}C NMR spectroscopy, and mass spectrometry.

EXPERIMENTAL

The ^1H, ^{19}F, and ^{13}C NMR spectra were taken at 20°C on a Bruker WR-200SY spectrometer at 200.13, 188.31, and 50.37 MHz, respectively. The chemical shifts are given relative to TMS (^1H and ^{13}C) and CF_3CO_2H (^{19}F, external standard). The mass spectra were taken on a YG-7070E mass spectrometer. The R_f values of the products were obtained on Silufol UV-254 plates with 1:1 CCl_4-acetone (A), 3:1 CCl_4-acetone (B), and 6:1 CCl_4-acetone (C) as the eluents.

Phenylhydrazone of Methyl Trifluoropyruvate (III). A sample of 2.02 g (II) was added to 1.08 g phenylhydrazine in 15 ml $CHCl_3$ and heated for 24 h at 80°C. The solvent was distilled off and the residue was crystallized from pentane to give 2.41 g (III). PMR spectrum* in CCl_4 (δ, ppm): 11.82 br.s (1H, NH), 6.61 m (4H, $H^{2,3,5,6}$), 6.21 m (1H, H^4), 3.20 s (3H, OCH_3). ^{19}F NMR spectrum in acetone (δ, ppm): −13.5 s. $^{13}C-\{^1H\}$ PMR spectrum in acetone: 161.68 (C=O), 142.3 (C^1), 129.9 ($C^{3,5}$), 125.1 (C^4), 120.0 (CF_3, $^1J_{C-F}$ = 277.2 Hz), 115.7 ($C^{2,6}$), 114.1 (C=N, $^2J_{C-N}$ = 32.8 Hz), 52.2 (OCH_3).

4-Nitrophenylhydrazone of Methyl Trifluoropyruvate (IV). A sample of 1.6 g (II) was added to 1.53 g 4-nitrophenylhydrazine in 50 ml chloroform in a sealed vessel and heated for 50 h at 80°C. The solvent was distilled off. The residue was dissolved in 20 ml acetone and poured into 1 liter water. The precipitate was filtered off to give 2.7 g (IV). PMR spectrum in acetone-d_6 (δ, ppm): 8.31 m (2H, $H^{2,6}$), 7.75 m (2H, $H^{3,5}$), 4.00 s (3H, OCH_3). ^{19}F NMR spectrum in acetone (δ, ppm): −12.8 s.

2(1-Hydroxy-1-trifluoromethyl-2,2,2-trifluoroethyl)phenylhydrazine (V). A sample of 1.08 g phenylhydrazine in 15 ml chloroform was placed into a sealed vessel and cooled to from −50 to −60°C. Then, 3.32 g (I) was condensed in and left for 24 h at 20°C. The precipitate formed was filtered off and washed with pentane to give 1.87 g (V). PMR spectrum in acetone-d_6 (δ, ppm): 6.80 m (1H, H^4), 7.31 m (2H, $H^{3,5}$), 7.65 m (1H, H^6), 8.42 br.s (1H, OH). ^{19}F NMR spectrum in acetone (δ, ppm): −4.05 s.

2-Amino-2′-(1-hydroxy-1-trifluoromethyl-2,2,2,-trifluoroethyl)diphenylamine (VI). A sample of 1.84 g hydrazobenzene in 20 ml chloroform was placed into a sealed vessel and

*The sample was prepared in freshly distilled CCl_4.

cooled to from −50 to −60°C. Then 1.72 g (I) was condensed in and left for 24 h at 20°C. The precipitate was filtered off and washed with pentane to give 0.87 g (VI). PMR spectrum† in acetone-d_6 (δ, ppm): 6.78 m (4H, $H^{4,5,4',5'}$), 7.42 m, 7.38 m, 7.50 m, 7.60 m (4H, $H^{3,6,3',6'}$). ^{19}F NMR spectrum in acetone (δ, ppm): 4.25 s. $^{13}C-\{^1H\}$ spectrum in acetone (δ, ppm): 128.2 ($C^{3',5'}$), 127.3 ($C^{3,5}$), 121.0 (CF_3, $^1J_{C-F}$ = 270.8 Hz), 120.0 ($C^{4,4'}$), 115.0 ($C^{6,6'}$), 72.2 ($-(CF_3)_2OH$), $^2J_{C-F}$ = 33.0).

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†The PMR spectrum consists of two strongly coupled ABCD KLMN systems without spin-spin coupling between them.