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C-ALKYLATION OF 3-METHYL-1-PHENYL-5-PYRAZOLONE BY HEXAFLUOROACETONE AND ITS IMINES

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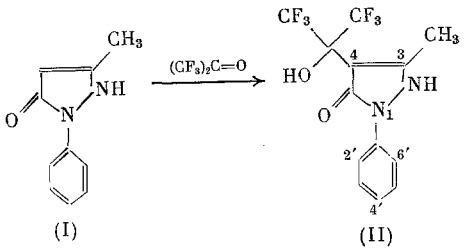
Some aromatic amines and heteroaromatic compounds react in the absence of catalyst with hexafluoroacetone [1-5] and its imines [6-8] to form C-alkylation products. In the present work, results are given for a study of the reactions of hexafluoroacetone and its imines with 3-methyl-1-phenyl-5-pyrazolone (I).

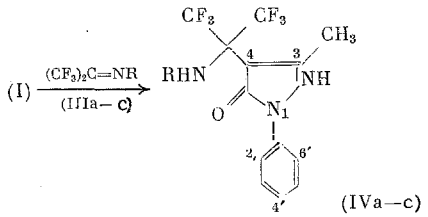
Pyrazolone (I) reacts with hexafluoroacetone quantitatively to give 4-(α-hydroxyhexafluoroisopropyl)-3-methyl-1-phenyl-5-pyrazolone (II).



(I) (II)

Thus, the alkylation is directed toward the site of maximum electron density in (I) [9].

Pyrazolone (I) reacts analogously at 20°C with the trifluoroacetylimine (IIIa) and benzenesulfonylimine (IIIb) of hexafluoroacetone. Imine (IIIa) was found to be more active than (IIIb), which was noted previously in reactions with indole [7]. The only reaction products were pyrazolones (IVa) and (IVb) which are the products of C^4-alkylation. Hexafluoroacetone imine (IIIc), whose electrophilicity is much less than that for N-acyl derivatives (IIIa) and (IIIb), reacts with (I) at 120°C to give 4-(α-aminohexafluoroisopropyl)-3-methyl-4-phenyl-5-pyrazolone (IVc) in 68%. Pyrazolone (IIIc) was obtained also by heating trifluoroacetyl derivative (IVa) in a water–ethanol solution of NaOH at reflux.



(IVa–c)

R = CF_3CO (IIIa), (IVa); R = $C_6H_5SO_2$ (IIIb), (IVb); R = H (IIIc), (IVc).

The structures of (II) and (IVa)-(IVc) were established using ^{13}C and ^{19}F NMR spectroscopy (Table 1) PMR spectroscopy (Experimental) and elemental analysis (Table 2). The multiplicity of the signals in the EMR spectra indicate the C^4-substitution of 3-methyl-1-phenyl-5-pyrazolone (I).

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TABLE 1. ^{13}C and ^{19}F NMR Spectra of (II) and (IVa)-(IVc) (δ, ppm) in Acetone

Compound	^{13}C *										^{19}F	$^{1}J_{CF}$, Hz
	3	4	5	1′	2′, 6′	3′, 5′	4′	CH_3	CF_3	C–CF_3		
(II)	145,8	90,1	162,5	133,8	119,5	128,1	125,8	10,8	122,5	75,5	−1,2 sec	285
(IVa)	149,3	89,4	162,4	135,9	122,3	130,1	128,0	14,0	123,9	67,8	−10,0 sec, −3,2 sec (2 : 1)	285
(IVb)	148,2	90,8	158,0	136,0	121,0	128,7	126,3	14,0	122,3	66,6	1,3 sec†	290
(IVc)	146,4	90,3	158,8	136,7	120,5	129,0	125,8	13,7	124,0	63,4	−4,1 sec	285

*The spectra of (IIIa) and (IIIb) also show signals for ^{13}C nuclei belonging to substituents R.
†Taken in DMSO.

TABLE 2. Products (I) and (IVa)-(IVc)

Compound	Yield, %	Mp, °C	R_f	Found / Calculated, %			Chemical formula
				C	H	N	
(II)	90,8	192	0,42	45,78 / 45,89	2,80 / 2,96	8,28 / 8,23	$C_{13}H_{10}N_2O_2F_6$
(IVa)	90,2	220 (dec.)	0,29	41,34 / 41,37	2,18 / 2,31	9,56 / 9,69	$C_{15}H_{10}N_3O_2F_9$
(IVb)	83,9	165 (dec.)	0,22	47,20 / 47,60	2,88 / 3,15	8,73 / 8,77	$C_{19}H_{15}N_3O_3SF_6$
(IVc)	a) 68,0 b) 77,0	142	0,53	46,45 / 46,03	2,96 / 3,27	11,96 / 12,38	$C_{13}H_{11}N_3OF_6$

EXPERIMENTAL

The ^1H, ^{19}F and ^{13}C NMR spectra were taken on a Bruker WP-200SY spectrometer at 200.13, 188.31 and 50.31 MHz, respectively, relative to TMS (^1H and ^{13}C) and external CF_3CO_2H (^{19}F). The R_f values were determined on Silufol UV-254 plates using 3 : 1 CCl_4–acetone as eluant. The spots were revealed with UV light. The preparative chromatography was carried out on plates with 2-mm unattached Chemapol LSL 5/40 μm silica gel layer. The charge on the plate was not more than 300 mg.

4-(α-Hydroxyhexafluoroisopropyl)-3-methyl-1-phenyl-5-pyrazolone (II). A sample of 6.60 g pyrazolone (I) and 20 ml abs. $CHCl_3$ were placed in a glass ampul and cooled to −600°C. A sample of 7.90 g hexafluoroacetone was condensed into this ampul , which was then sealed and left at 20°C. After 16 h, the solvent and excess hexafluoroacetone were removed in vacuum. The residue was recrystallized from toluene to yield 11.50 g (III). PMR spectrum in acetone-d_6 (δ, ppm): 2.35 s (3H, CH_3), 7.32 m (1H, C^4–H), 7.42 m (2H, $C^{3'}$–H, $C^{5'}$–H), 7.63 m (2H, $C^{2'}$–H, $C^{6'}$–H).

4-(α-Trifluoroacetamidohexafluoroisopropyl)-3-methyl-1-phenyl-5-pyrazolone (IVa). A sample of 3.5 g (IIIa) was added with stirring to a suspension of 2.3 g (I) in 15 ml abs. $CHCl_3$ at −40°C and left for 4 h at 20°C. The precipitate was filtered off and crystallized from chloroform–ethyl acetate to give 4.51 g (IVa).

4-(α-Benzenesulfonylamidohexafluoroisopropyl)-3-methyl-1-phenyl-5-pyrazolone (IVb). A sample of 4.0 g (IIIb) was added to a suspension of 2.3 g pyrazolone (I) in 10 ml abs. $CHCl_3$ at −40°C and left for 48 h at 20°C. The solvent was evaporated in vacuum and the residue was crystallized from ether to give 5.2 g (IVb).

4-(α-Aminohexafluoroisoprop-2-yl)-3-methyl-1-phenyl-5-pyrazolone (IVc). a) A sample of 2.4 g (I) and 10 ml abs. $CHCl_3$ were placed in a glass ampul and cooled to 0°C. A sample of 3.2 g (IIIc) was added. The ampul was sealed and heated for 10 h at 120°C. After cooling, the reaction mixture was evaporated. The residue was subjected to chromatography on silica gel plates and recrystallized from CCl_4 to give 3.2 g (IVc). PMR spectrum in DMSO–d_6 (δ, ppm): 2.20 s (3H, CH_3), 7.25 m (1H, $C^{4'}$–H), 7.47 m (2H, $C^{3'}$–H, $C^{5'}$–H), 7.55 m (2H, $C^{2'}$–H, $C^{6'}$–H).

b) A sample of 0.8 g in 30 ml 1 M NaOH in 2 : 1 ethanol–water was heated at reflux for five days. The mixture was cooled, neutralized with 1 M hydrochloric acid, and extracted with 50 ml chloroform. The extract was washed with water, dried over Na_2SO_4, and evaporated. The residue was recrystallized from CCl_4 to give 480 mg (IVc).

CONCLUSIONS

Regiospecificity was demonstrated for C-alkylation in the reactions of 3-methyl-1-phenyl-5-pyrazolone with hexafluoroacetone and the trifluoroacetylimine and benzenesulfonylimine of hexafluoroacetone at C^4 of the heterocycle.

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MECHANISM OF THE REACTION OF CUPROUS DIALKYLTHIOPHOSPHATES WITH HALOACETYLENES

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Substituted ethynyl halides do not undergo nucleophilic substitution with salts of dialkylthiophosphoric acid [1] since the halogen atom is "positive" in haloacetylenes as in hypohalites [2]. On the other hand, such haloacetylenes readily react with the cuprous salts of these acids to form S-ethynylthiophosphates. In contrast to the analogous potassium salts of dialkylthiophosphoric acids, the cuprous salts do not react with haloalkanes [3]. Hence, the mechanism of the ethynylation of cuprous dialkylthiophosphates presumably differs radically from that for alkylation by potassium dialkylthiophosphates.

In the present work, we studied the mechanism of the reaction of the cuprous salts of dialkylthiophosphoric acids with substituted ethynyl halides in the case of the reaction of phenylbromoacetylene (PBA) with cuprous O,O-diethylthiophosphate

$$(C_2H_5O)_2PSOCu + BrC{\equiv}CPh \rightarrow (C_2H_5O)_2P(O)SC{\equiv}CPh \quad (1)$$

The chemical shift for the phosphate atom in the ^{31}P NMR spectrum of this salt is 38.26 ppm (H_3PO_4 as standard). Upon the addition of excess PBA, the ^{31}P NMR signal disappeared and reappeared after several days at 16.6 ppm, which corresponds to the ^{31}P NMR spectrum of O,O-diethyl-S-phenylethynylthiophosphate (I). Apparently, a paramagnetic intermediate species is formed in the reaction mixture which disappears toward the end of the reaction. Indeed, ESR spectroscopy indicated the formation of paramagnetic cupric species in the reaction of cuprous diethylthiophosphate with PBA. The ESR spectrum of the reaction recorded at 77°K is given in Fig. 1.

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