REACTION OF 1-METHYLPYRAZOLES WITH AROMATIC ACID CHLORIDES

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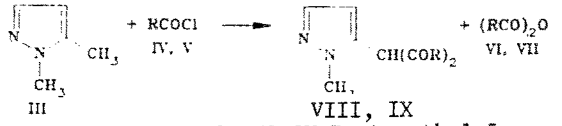
1-Methylimidazole [1] and 4,5-dimethylthiazole [2] react with aromatic acid chlorides in the presence of triethylamine to form 2-aroyl-substituted derivatives.

We have studied the behavior of 1-methylpyrazoles I-III under these conditions. When heated with benzoyl chloride (IV) or 1-methylpyrazol-5-oyl chloride (V) in acetonitrile and subsequent treatment with triethylamine, compounds I and II give as the sole products the anhydrides of benzoic acid (VI) or 1-methylpyrazole-5-carboxylic acid (VII). Reaction of the dimethylpyrazole III with IV or V also did not lead to acylation of the pyrazole ring but to a mixture of the 5-diaroylmethyl-1-methylpyrazoles VIII or IX together with the anhydride VI or VII.



IV, VI, VIII R=C_6H_5; V, VII, IX R=1-methyl-5-pyrazolyl

According to the PMR spectrum of the product, the reaction of pyrazole III with V also leads to formation of a small amount (~5%) of the monoaroylation product 1,2-bis(1-methylpyrazol-5-yl)ethanone (X).

Acid chloride V (7.2 g, 0.05 mole) was added to a solution of III (6.8 g, 0.07 mole) in acetonitrile (40 ml), refluxed for 8 h, cooled, and triethylamine (5 g, 0.05 mole) added dropwise. The reaction product was refluxed for 3 h, cooled, the precipitate filtered off, and the solvent evaporated. The residue was treated with sodium carbonate (5%, 50 ml) and extracted with chloroform. After distillation of solvent the residue was chromatographed on silica gel (eluent chloroform–ethanol, 20:1) to give anhydride VII (0.7 g, 12%) and (1.1 g, 15%) 5-[bis(1-methylpyrazole-5-carbonyl)methyl]-1-methylpyrazole (IX).

Compound VII. mp 106-107°C (from hexane). PMR spectrum (DMSO-D_6, TMS standard): 4.12 (3H, s, CH_3); 6.83 (1H, d, J = 2 Hz, 4-H); 7.50 ppm (1H, d, J = 2 Hz, 3-H). Mass spectrum: M^+ 234.

Compound IX. mp 128-130°C (petroleum ether–chloroform, 1:1). PMR spectrum (DMSO-D_6, TMS): 3.90, 3.93, 4.01 (each 3H, s, CH_3); 6.34 (1H, d, J = 2 Hz, 4'-H); 6.53 (1H, d, J = 2 Hz, 4"-H); 6.90 (1H, s, CH); 7.23 (1H, d, J = 2 Hz, 4-H); 7.35 (1H, d, J = 2 Hz, 3'-H); 7.38 (1H, d, J = 2 Hz, 3"-H); 7.61 ppm (1H, d, J = 2 Hz, 3-H). Mass spectrum: M^+ 312.

The PMR spectrum of the residue before chromatography also shows signals for X ($CDCl_3$, HMDS standard): 4.09 (3H, s, CH_3); 4.14 (2H, s, CH_2); 6.09 (1H, d, J = 2 Hz, 4-H); 6.86 (1H, d, J = 2 Hz, 4'-H); 7.37 (1H, d, J = 2 Hz, 3-H); 7.44 ppm (1H, d, J = 2 Hz, 3'-H).

Similar reaction of III with benzoyl chloride gave **benzoic anhydride** (mp 40-42°C, 13% yield, mass spectrum: M^+ 226) and **5-dibenzoylmethyl-1-methylpyrazole (VIII)**, (mp 106-107°C, from 2-propanol, 34%). PMR spectrum for VIII (DMSO-D_6, TMS): 3.97 (3H, s, CH_3); 6.30 (1H, d, J = 2 Hz, 4-H); 7.16 (1H, s, CH); 7.24-7.80 (m, 9H, Ph + 3-H); 8.06-8.32 ppm (m, 2H, Ph). Mass spectrum: M^+ 304.

Elemental analytical data for the synthesized materials was in agreement with that calculated.

LITERATURE CITED

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