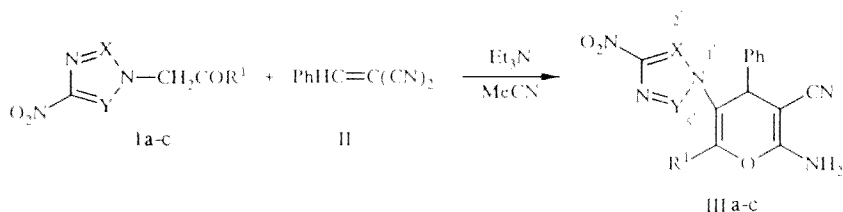


SYNTHESIS OF 2-AMINO-5-(N-AZOLYL)PYRANS

A. V. Samet, A. M. Shestopalov, and V. V. Semenov

2-Aminopyrans are of interest for practical use [1] and as intermediates in the synthesis of heterocycles [2]. One of the main methods for their production is the reaction of β -dicarbonyl compounds with unsaturated nitriles [1]. At the same time, the reaction of the latter with monocarbonyl compounds takes place differently. Thus, N-phenacylpyridinium salts give cyclopropanes in reaction with arylidenemalononitriles in the presence of bases [3].

In contrast to this, the reaction of N-acetyl- and N-phenacylazoles (Ia-c) with the benzylidenemalononitriles (II) that we studied unexpectedly leads to previously unknown (N-azolyl)-substituted pyrans (IIIa-c). The reaction takes place in acetonitrile in the presence of catalytic amounts of triethylamine at room temperature.



I, III a X = Y = N, R¹ = Me; b X = CH, Y = N, R¹ = Me; c X = Y = CH, R¹ = Ph

The PMR spectra were recorded in acetone-d₆, and the IR spectra were recorded in tablets with potassium bromide.

2-Amino-6-methyl-5-(5-nitro-2-tetrazolyl)-4-phenyl-4H-pyran-3-carbonitrile (IIIa). Calculated, %: C 51.69, H 3.42, N 30.14. C₁₄H₁₁N₇O₃. Found, %: C 51.43, H 3.60, N 29.89. The yield was 55%; mp 169-170°C (decomp.). PMR spectrum (δ , ppm): 2.10 (3H, s, Me), 4.81 (1H, s, 4-H), 6.48 (2H, bs, NH₂), 7.2-7.3 (5H, m, H_{Ph}). IR spectrum, cm⁻¹: 3440, 3325 (ν_{NH_2}), 2210 (ν_{CN}), 1635 (ν_{NH_2}), 1565, 1310 (ν_{NO_2}).

2-Amino-6-methyl-5-(3-nitro-1,2,4-triazol-1-yl)-4-phenyl-4H-pyran-3-carbonitrile (IIIb). Calculated, %: C 55.55, H 3.74, N 25.91. C₁₅H₁₂N₆O₃. Found, %: C 55.63, H 3.79, N 26.05. The yield was 69%; mp 244-245°C (decomp.). PMR spectrum (δ , ppm): 1.97 (3H, s, Me), 4.59 (1H, s, 4-H), 6.39 (2H, bs, NH₂), 7.3-7.45 (5H, m, H_{Ph}), 8.35 (1H, s, 5'-H). IR spectrum, cm⁻¹: 3470, 3330 (ν_{NH_2}), 2195 (ν_{CN}), 1635 (ν_{NH_2}), 1550, 1310 (ν_{NO_2}).

2-Amino-5-(4-nitro-1-imidazolyl)-4,6-diphenyl-4H-pyran-3-carbonitrile (IIIc). Calculated, %: C 65.44, H 3.93, N 18.17. C₂₁H₁₅N₅O₃. Found, %: C 65.57, H 4.02, N 18.13. The yield was 52%; mp 123-126°C (decomp.). PMR spectrum (δ , ppm): 4.73 (1H, s, 4-H), 6.52 (2H, bs, NH₂), 7.3-7.5 (10H, m, H_{Ph}), 7.27 (1H, bs, 2'-H), 7.96 (1H, bs, 5'-H). IR spectrum, cm⁻¹: 3315 (ν_{NH_2}), 2200 (ν_{CN}), 1645 (ν_{NH_2}), 1540, 1295 (ν_{NO_2}).

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