In contrast, triacetate X is formed from compounds IVa and Va after prolonged heating with acetic anhydride, but like acetates VIII and IX, it readily loses the acetyl group and converts into diacetate XI.

The primary loss of nitrogen [$M^+ - 28$] is not characteristic of the mass spectra of all the compounds synthesized, and therefore the above structures with 2H-triazole fragment are most probable for the solid state [4].

In the PMR spectra ($CDCl_3$) of compounds IVa-d, as in the previously described vic-triazoles [5], the NH group of the triazole ring is represented by a very weak-field singlet (~15-16 ppm), while the amide NH group is bound by an intramolecular hydrogen bond to the ketonic carbonyl and appears at 11.28 ppm (compared with 10.10 ppm in DMSO-D_6).

For compounds IX, X with an acetyl group in the triazole ring, a signal of this group at 2.83-2.85 ppm is characteristic, while the amide acetyl appears in the stronger field at 2.25 ppm.

We compared the IR and PMR spectra and certain chemical properties of 2-acetyltriazoles [2, 3] and of compounds VIII-X, and ascribed to the latter structures with the acetyl group at the 2-position of the triazole ring.

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REACTION OF 1-TOSYLOXYAZIRIDINE-2,2-DIACARBOXYLIC ESTER WITH TRIETHYLAMINE

A. V. Prosyanik, P. N. Belov, and V. I. Markov

UDC 547.717'461.3+547.787.1'29

Aziridines react with nucleophilic reagents due to the presence of a readily removable electronegative group at the nitrogen atom. Thus, 1-tosyloxy-2,2-bis(trifluoromethyl)aziridine reacts with alkyl- and dialkylamines with ring opening and the formation of N-hexafluoroisopropylformamidines [1, 2], while treatment of this aziridine by sodium cyanide leads to 2,2-bis(trifluoromethyl)-3-cyanoaziridine [2].

We found that when 1-tosyloxyaziridine-2,2-dicarboxylic ester [3] is boiled for 30 min with triethylamine in benzene, the ethyl ester of 5-ethoxyoxazole-4-carboxylic acid is unexpectedly formed, while 1-acetyloxyaziridine-2,2-dicarboxylic ester [3] is inert in this reaction, even on boiling for 4 h.

As in [2], the formation of oxazole can be described via an intermediate azirine-2,2-dicarboxylic ester. However, when this reaction was carried out in methanol, we were unable to detect the presence of 3-methoxyaziridine-2,2-dicarboxylic ester, a product of the addition of methanol to azirine. This can probably be explained by its short lifetime as the result of thermodynamically favorable rearrangement into oxazole. The 1-acetyloxyaziridine-2,2-dicarboxylic ester is inert because the AcO^- group must be eliminated, and this electronegative group is much less readily removed than TsO^- in the formation of the intermediate azirine.

F. É. Dzerzhinskii Dnepropetrovsk Chemical Engineering Institute, Dnepropetrovsk 320005.

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Oxazole: yield 74-80%, bp 95-96°C (0.5 mm), n_D^{20} 1.4774. IR spectrum: 1735 (C=O), 1625 (C=N), 1535 cm^{-1} (C=C). PMR spectrum (CCl_4): 1.30 and 1.40 (CH_3, t, J = 7.5 Hz), 4.17 and 4.40 (CH_2, quart), 7.35 ppm (H, s). Found: N 7.7%. $C_8H_{11}NO_4$. Calculated: N 7.6%.

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CONDENSED PYRANOISOQUINOLINES

Yu. M. Volovenko, V. A. Litenko, and F. S. Babichev

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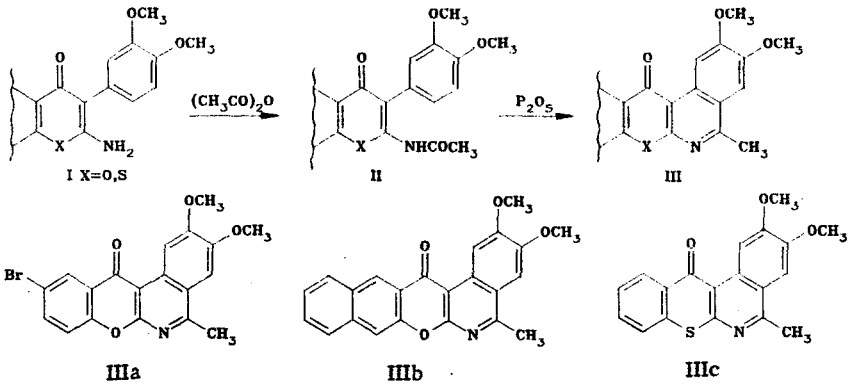
The acylation of 4H-2-amino-3-(3,4-dimethoxyphenyl)areno[b]pyran-4-ones (I) by acetic anhydride in pyridine leads to the corresponding N-acetyl derivatives (II) [1]. Treatment of the latter with phosphoric anhydride in chlorobenzene (boiling for 8-12 h) is accompanied by cyclodehydration and the formation of an isoquinoline ring. Derivatives of new heterocyclic polynuclear systems were thus obtained: benzo[5,6]pyrano-[2,3-c]isoquinoline (IIIa), naphtho[2',3'-5,6]pyrano[2,3-c]isoquinoline (IIIb) and benzo[5,6]-1-thiapyrano[2,3-c]isoquinoline (IIIc).



Data of elemental analysis correspond to the empirical formulas: $C_{19}H_{14}BrNO_4$ [IIIa, mp 285°C (from DMFA)], $C_{23}H_{17}NO_4$ [IIIb, mp 317-318°C (from DMFA)], $C_{19}H_{15}NO_3S$ [IIIc, mp 256°C (from DMFA)]. In the IR spectra of the compounds obtained, the pyran ring carbonyl group absorbs at 1660-1650 cm^{-1}, and there is no absorption above 3050 cm^{-1}. Of the two possible cyclization paths, only one exists: The isomer shown in the scheme is formed, as confirmed by the presence of a one-proton singlet at 9.7 (1-H) and 7.8 ppm (4-H) in the PMR spectra of compounds III (in CF_3COOD).

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T. G. Shevchenko Kiev State University, Kiev 252017.

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