LETTERS TO THE EDITOR

NEW METHOD OF CONVERTING 1-ACETYLINDOLIN-3-ONE AND AROMATIC ALDEHYDES INTO o-AMINOPHENYL KETONES OF THE vic-TRIAZOLE SERIES

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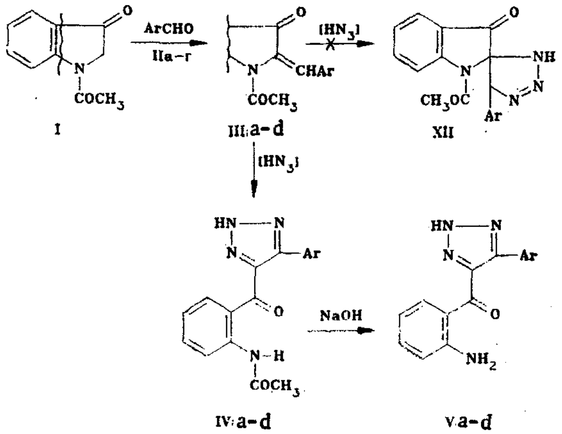
We found that 1-acetyl-2-arylideneindolin-3-ones (IIIa-d) are converted into o-acetylaminobenzoyltriazoles IVa-d by the action of sodium azide in a 1:5 mixture of DMSO and acetic acid. The reaction is carried out with heating for 1 h, and the yield of compounds IVa-d is 87-90%; for IVa mp 195-196°C, M^+ 306. Under similar conditions, free 2-arylideneindolin-3-ones (VIa-d) do not enter into this reaction. The reaction proceeds only in the above mixture. If only acetic acid is used, the initial compounds IIIa-d become deacetylated on heating to compounds VIa-d.



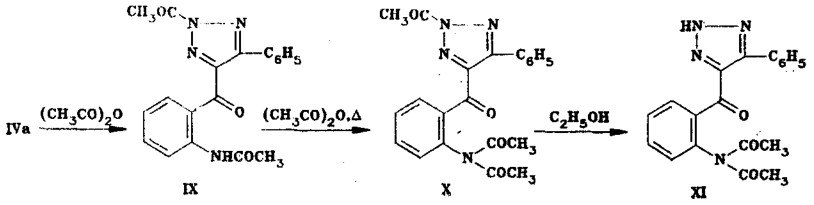
II—V a Ar=C_6H_5; Ar=*p-iso*-$C_3H_7C_6H_4$; Ar=*p*-$NO_2C_6H_4$; Ar = 4-pyridyl

The acetyl group of compounds IVa-d is readily removed on heating with 20-30% aqueous dioxane (2:1) solution of NaOH, and the yield of compounds Va-d is 95-97%. The initial compounds IIIa-d are readily formed from indolinone I and aldehydes IIa-d on heating in benzene with a catalytic amount of piperidine.

The presence of an ortho-aminobenzoyl grouping in compounds Va-d was shown in the case of Va by its oxidation with iodosobenzene diacetate to the corresponding anthranyl, mp 196-197°C, M^+ 262 [1].

The structure of triazoline XII isomeric with triazoles IV is not considered because of the absence of methine proton signals in the PMR spectrum.

The presence of a triazole fragment in compounds IVa-d, Va-d, VII was confirmed by certain transformations and spectral features, characteristic of vic-triazoles [2]. Compounds IVa and VII are readily acylated (acetic anhydride 20°C) to acetates VIII, IX. The latter, like N-acetyltriazoles already described [3], are deacetylated to initial VII, IVa, even when they dissolve in alcohol.



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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

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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.

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