CONDENSATION OF 1-ARYL-5-METHYLTETRAZOLES WITH ALDEHYDES

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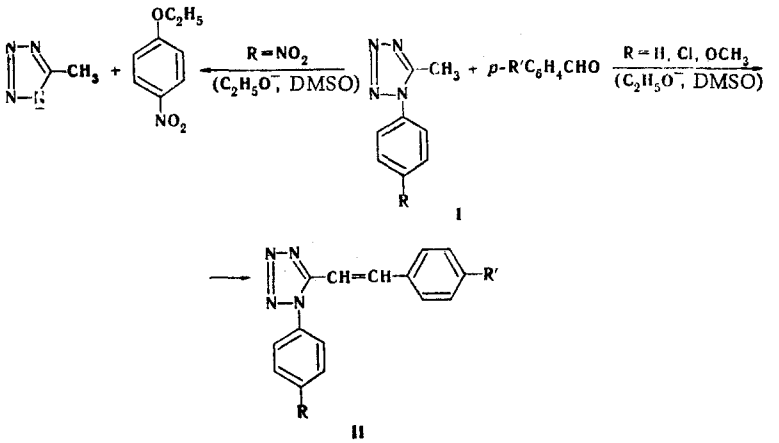
The ability to undergo condensation with aldehydes to give ethylene compounds is characteristic for heteroaromatic compounds with a methyl group. C-Methyltetrazoles constitute an exception. Thus 1-phenyl-5-methyltetrazole (I) does not react with benzaldehyde even under severe conditions [1] (heating with $ZnCl_2$ at 200°C). According to our data, tetrazole I does not react with benzaldehyde in an alcohol solution of sodium ethoxide or when it is heated with acetic anhydride, i.e., the conditions under which picolines or quinaldine react smoothly.

However, in the presence of dimethyl sulfoxide (DMSO) or dimethylformamide (DMF) I undergoes condensation with aromatic aldehydes at room temperature, and the products are obtained in 60-80% yields. These solvents evidently disrupt the solvate formed between the ethoxide anion and the alcohol, and this facilitates deprotonation of the methyl group [2] and increases the rate of reaction of the aldehyde with the resulting carbanion. We used this method to obtain a series of α-[1-(4-R-phenyl)-5-tetrazolyl]-β-(4-R'-phenyl)ethylenes (II). For example, solution of 1.4 g (0.01 mole) of benzaldehyde in 10 ml of DMSO was added gradually at room temperature with stirring to 1.6 g (0.01 mole) of tetrazole I in 15 ml of DMSO and 0.23 g (0.01 mole) of Na in 2.5 ml of absolute ethanol. After 2 h, the mixture was neutralized with 1 ml of acetic acid, and the condensation product was precipitated by the addition of water and crystallized from alcohol. The following compounds were obtained by this method (R and R', yield in percent, and melting point in degrees centigrade given): H, H, 88, 182-183; H, Cl, 85, 152-153; H, $N(CH_3)_2$, 60, 115-116; Cl, H, 90, 142-143; Cl, Cl, 95, 213-215; Cl, $N(CH_3)_2$, 50, 155-156; OCH_3, H, 60, 99-100; OCH_3, Cl, 65, 160-161; OCH_3, $N(CH_3)_2$, 37, 139-140. 1-(1-Phenyl-5-tetrazolyl)-4-phenylbutadiene (III), with mp 160-161°C, was obtained in 35% yield, and 1-[1-(p-chlorophenyl)-5-tetrazolyl]-4-phenylbutadiene (IV), with mp 195-196°C, was obtained in 75% yield by similar reactions with cinnamaldehyde.



I

II

4-Nitrophenetole (75% yield) and 5-methyltetrazole were isolated unexpectedly instead of α,β-substituted ethylene in the reaction of 1-(4-nitrophenyl)-5-methyltetrazole with the aldehyde. Nucleophilic substitution of the tetrazole ring by ethoxide ion is evidently explained by a strong positive charge on the phenyl carbon atom bonded to the heteroring nitrogen atom and the stability of the departing 5-methyltetrazole anion.

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The results of elementary analysis of the compounds obtained in this research are in agreement with the calculated values. According to the PMR spectra of II in $CDCl_3$, they have trans structures (J = 16 Hz).

LITERATURE CITED

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2. D. J. Cram, Fundamentals of Carbanion Chemistry, Academic Press (1965).

SPLITTING OUT OF AN ACYL GROUP IN THE RECYCLIZATION OF THE PYRIDINE RING TO A BENZENE RING

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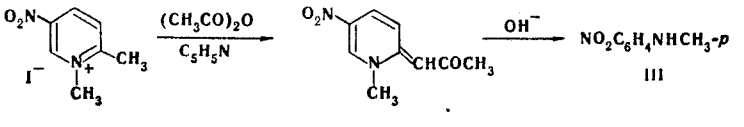
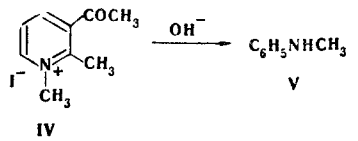
We have previously shown that nitropicolinium salts under the influence of bases undergo opening of the pyridine ring with subsequent closing at the α-methyl group to give the corresponding nitroanilines [1]. It might have been expected that activation of the α-methyl group by an acceptor substituent would increase its CH acidity and thus promote the formation of a benzene ring in the step involving opening of the intermediate. However, it was found that the anhydro base (II) obtained from 2-methyl-5-nitropyridine methiodide (I) readily splits out an acyl fragment to give N-methyl-4-nitroaniline (III). Thus nitroaniline III (mp 148-149°C), identical to an authentic sample, was obtained in 35% yield (after preparative chromatography on silica gel in chloroform) in the reaction of a 25% aqueous solution of methylamine with anhydrobase II for 24 h. In contrast to the usually labile α-anhydro bases, anhydro base II is characterized by high stability; this is probably explained by the effect of acceptor substituents. Base II was obtained by refluxing 2-methyl-5-nitropyridine methiodide (I) with acetic anhydride in pyridine for 1 h. The product was obtained in 45% yield (after preparative chromatography on silica gel in ethyl acetate) and had mp 206-207°C (from chloroform). UV spectrum (in $CHCl_3$): λ_{max} 279 and 405 nm (log ε 3.57 and 4.42). PMR spectrum (in $CDCl_3$), δ: 8.63 (d, 3-H, J_{34} = 10 Hz), 8.36 (d, 6-H, J_{46} = 2 Hz), 7.58 (m, 4-H), 5.26 (s, CH), 3.48 (s, NCH_3), and 2.16 ppm (s, CH_3CO).

It is interesting that if the acyl group is located in the ring, opening of this pyridine ring takes place readily, but in this case also the competitive removal of an acyl group turns out to be preferred, so that the final product is N-methylaniline (V). Thus N-methylaniline, identical to an authentic sample, was obtained in 26% yield when 2-methyl-3-acetylpyridine (IV) was headed at 200°C with a mixture of 25% aqueous methylammonium bisulfite for 30 h.





Thus recyclization to anilines with acidic splitting out of an acetyl group takes place in the reaction of bases with pyridine derivatives that contain both exocyclic and endocyclic

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