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HETEROCYCLIZATION OF 1-(2'-CARBETHOXYPHENYL)-5-METHYLTETRAZOLE

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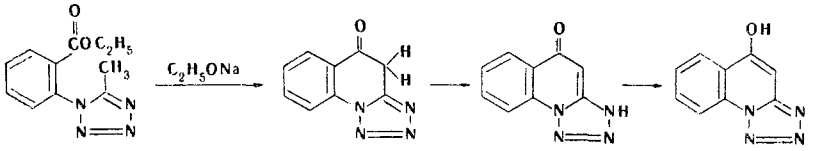
1-(2'-Carbethoxyphenyl)-5-methyltetrazole is converted to 5-hydroxytetrazolo-[1,5-*a*]quinoline when it is heated in dimethyl sulfoxide and dimethylformamide with sodium ethoxide. The hydroxy structure of the compound obtained was confirmed by spectral methods.

The methyl group of 1-aryl-5-methyltetrazole is distinguished by its inertness in reactions involving condensation with electrophilic reagents [1] under conditions for which other heteroaromatic compounds with a similar orientation of the methyl group attached to an azomethine bond (for example, picolines and 2-methylimidazoles) are active.

We have recently shown that methyltetrazoles can nevertheless be successfully used in aprotic polar solvents in reactions with electrophilic reagents such as aryl aldehydes [2]. It is also known [1] that 1-phenyl-5-methyltetrazole reacts in the presence of sodium ethoxide with excess diethyl oxalate to give a product of ester condensation.

These data enabled us to suggest the possibility of the realization of intramolecular ester condensation — heterocyclization — of 1-(2'-carbethoxyphenyl)-5-methyltetrazole (I) with the formation of the as yet unknown tetrazolo [1,5-*a*]quinol-5-one.

We found that a compound with an elementary composition corresponding to proposed structure II is formed in almost quantitative yield when ester I is heated with sodium ethoxide in dimethylformamide (DMF).



I IIa IIb IIc

Product II was obtained in 70% yield when the reaction was carried out in dimethyl sulfoxide (DMS), whereas it was obtained in only 22% yield in ethanol, and the remaining ester I underwent hydrolysis.

The IR spectra of II recorded in mineral oil and trifluoroacetic acid do not contain absorption bands at 2100 cm^{-1}, and this indicates the absence of the azide form. The same thing is also characteristic for unsubstituted tetrazolo[1,5-*a*]quinoline [3]. Absorption bands corresponding to vibrations of an NH group (3200-3300 cm^{-1}) also were not observed in the spectra recorded in mineral oil, KBr pellets, tetrahydrofuran (THF), and chloroform; this excludes structure IIb. At the same time, the IR spectra contain a broad absorption band at 1620-1630 cm^{-1}, which can be assigned to vibrations of a carbonyl group or a C=N bond. An acetyl derivative was obtained when II was heated with acetic anhydride, while a methyl derivative was obtained in the reaction with dimethyl sulfate. Methylation and acylation of II are possible at both the nitrogen (IIb) and oxygen (IIc) atoms.

It is known that the NCH_3 and OCH_3 groups can be distinguished unambiguously from PMR data [4]. The signal of a methyl group in the spectrum of the methylation product (δ = 4.17

*Deceased.

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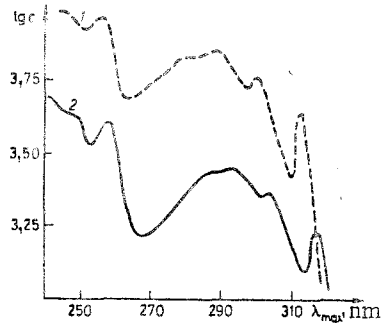

Fig. 1. Electronic spectra of 5-hydroxy-(II) (1) and 5-methoxytetrazolo[1,5-*a*]-quinoline (III) (2) in ethanol.

ppm) is found at even weaker field than, for example, in the spectrum of the previously described 1-methyl-4-methoxy-2-quinolone (δ_{OCH_3} = 3.92 ppm) [5]. These data show that 5-methoxytetrazolo[1,5-*a*]quinoline (III) is formed as a result of methylation of II, while acetoxy derivative IV was consequently obtained by acetylation. As in the case of the starting compound, the IR spectra of these compounds contain a strong band at 1620 cm^{-1}, which can thus be assigned to vibrations of a C=N bond. A distinct carbonyl band of an acetyl group at 1783 cm^{-1} is present in the spectrum of acetyl derivative IV.

The UV spectra of methoxy and acetoxy compounds III and IV, which are derivatives of hydroxy form IIc, in ethanol and THF coincide satisfactorily with the spectrum of starting II (Fig. 1). Thus the 5-hydroxytetrazolo[1,5-*a*]quinoline (IIc) structure should be assigned to the latter. The PMR data (singlet, 4H, δ = 6.89 ppm; complex multiplet of aromatic protons at 7.5-8.5 ppm; broad signal of OH proton at weak field, δ = 11.9 ppm) confirm the structure of quinoline II and indicate that the substance exists in hydroxy form IIc in DMSO. The rare (for quinoline) hydroxy structure is evidently associated with the annelated tetrazole ring; the distribution of multiple bonds in IIc coincides with that in the known 4-hydroxy-2-quinolone [6].

In conformity with this structure, II undergoes diazo coupling with the 4-nitrobenzenediazonium ion, evidently in the ortho position relative to the hydroxy group to give an azo dye.

The instance of heterocyclization presented in this paper is a variant of the Dieckmann intramolecular condensation to give, in this case, a quinoline ring; this may be of definite interest, since a number of previously described tetrazoloquinoline derivatives display fungicidal and bactericidal activity [7].

EXPERIMENTAL

The PMR spectra of solutions of the compounds in DMSO were recorded with a Perkin-Elmer R-12B spectrometer (60 MHz). The IR spectra of mineral oil suspensions, KBr pellets, and solutions in THF, chloroform, and trifluoroacetic acid were recorded with a UR-20 spectrometer. The UV spectra of solutions in ethanol and THF were measured with a Specord UV-vis spectrophotometer.

1-(2'-Carbethoxyphenyl)-5-methyltetrazole (I). A 3.8-g (72.4 mmole) sample of sodium acetate was added to a solution of the diazonium salt obtained from 10 g (72.8 mmole) of anthranilic acid, 5 g (72 mmole) of $NaNO_2$, and 60 ml of HCl (1:5), and the resulting mixture was added with stirring to a solution of 8.45 g (72.8 mmole) of diacetylhydrazine in 120 ml of 1 N Na_2CO_3 at −5°C. After 1 h, 150 ml of 5 N NaOH was added in portions, and the mixture was allowed to stand for 1 h. The pH of the mixture was adjusted to two, and the mixture was filtered to give 13,2 g (74%) of colorless crystals of 1-(2'-carboxyphenyl)-5-methyltetrazole with mp 171-172°C (dec., from butyl acetate). The product was identical to the product previously obtained by a less convenient method [8] (mp 172-173°C [8]). Ester I was obtained by refluxing the acid in ethanol saturated with HCl and had mp 100-101°C (from ethanol). Found: C 56.8; H 5.2; N 23.9%. $C_{11}H_{12}N_4O_2$. Calculated: C 56.9; H 5.2; N 24.1%.

5-Hydroxytetrazolo[1,5-*a*]quinoline (II). A 5 g (26.8 mmole) sample of ester I was dissolved in 60 ml of DMSO, a solution of sodium ethoxide (1.15 g of Na in 15 ml of absolute ethanol) in 40 ml of DMSO was added, and the mixture was stirred at 80°C for 3 h. It was then cooled to room temperature and treated with 3 ml of CH_3COOH and 100 ml of water. The mixture was filtered to give 2.65 g (70%) of 5-hydroxytetrazolo[1,5-*a*]quinoline as colorless needles with mp 236-237°C (dec., from ethanol). Found: C 58.2; H 3.5; N 30.0%. $C_9H_6N_4O$. Calculated: C 58.1; H 3.2; N 30.1%.

5-Methoxytetrazolo[1,5-*a*]quinoline (III). A 0.76-g (6 mmole) sample of dimethyl sulfate was added to a solution of 1.13 g (6 mmole) of II in a solution of 0.25 g of NaOH in 50 ml of water, and the mixture was heated at 80°C for 2 h. The precipitate was removed by filtration and suspended in dilute alkali. The suspension was then filtered to give 0.31 g (25%) of needles of the methoxy derivative with mp 219-220°C (dec., from ethanol). Found: C 59.8; H 4.2; N 27.6%. $C_{10}H_8N_4O$. Calculated: C 60.0; H 4.0; N 28.0%.

5-Acetoxytetrazolo[1,5-*a*]quinoline (IV). A 0.5-g (2.7 mmole) sample of II was refluxed in 5 ml of acetic anhydride, after which the excess anhydride was removed to give 0.6 g (98%) of the reaction product. Crystallization from ethanol gave colorless needles with mp 172-173°C. Found: C 58.0; H 3.6; N 24.8%. $C_{11}H_8N_4O_2$. Calculated: C 57.9; H 3.5; N 24.6%.

4-(4'-Nitrophenylazo)-5-hydroxytetrazolo[1,5-*a*]quinoline. A solution of 5 mmole of 4-nitrobenzenediazonium chloride was added at room temperature with stirring to a solution of 0.93 g (5 mmole) of II in 20 ml of 0.75 N Na_2CO_3 solution, and the mixture was worked up to give orange crystals of an azo dye with mp>300°C (from DMF). The yield was almost quantitative, and the product had λ_{max} 456 nm (ε $2.1 \cdot 10^5$) in DMSO. Found: C 53.5; H 2.7; N 29.0%. $C_{15}H_9N_7O_3$. Calculated: C 53.7; H 2.7; N 29.2%.

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