THE ACTION OF A NITRATING MIXTURE ON BENZO-1,5-DIAZEPINE

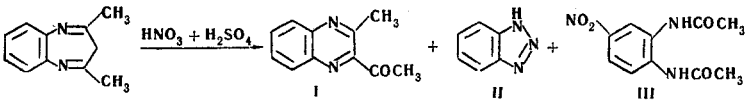
K. V. Levshina, L. P. Glazyrina, and
T. S. Safonova

UDC 547.892'863'791.8:543.422

It has been shown that the action of a mixture of nitric and sulfuric acids on 2,4-dimethylbenzo-1,5-diazepine leads to processes of nitration, hydrolytic cleavage, and oxidation with simultaneous isomerization, with the formation of N,N'-diacetyl-4-nitro-1,2-phenylenediamines, benzotriazole, and 2-acetyl-3-methylquinoxaline.

The action of electrophilic reagents on benzo-1,5-diazepine has been studied little. There is a paper [1] in which it is reported that in an attempt to nitrate 2,4-dimethyl-3H-benzo-1,5-diazepine it was impossible to isolate individual compounds, since the process was accompanied by pronounced resinification.

We have established that 2,4-dimethylbenzo-1,5-diazepine undergoes far-reaching transformations under the action of a mixture of nitric and sulfuric acid with the formation of 2-acetyl-3-methylquinoxaline (I), benzotriazole (II), and N,N'-diacetyl-4-nitro-1,2-phenylenediamine (III) with yields of 26, 8, and 40%, respectively.



I II III

The structure of substance I was confirmed by spectroscopy (the presence in the IR spectrum of an absorption band of a CO group at 1695-1705 cm^{-1} and the presence of a maximum in the UV region at 244 nm) and also by its similarity in elementary composition and melting point to a sample of 2-acetyl-3-methylquinoxaline [2] obtained by the oxidation of 2,4-dimethylbenzo-1,5-azepine with peracetic acid. The formation of a compound with a quinoxaline structure in this reaction shows that oxidative processes take place in it.

The formation of benzotriazole under the conditions of the reaction considered is apparently the result of the reaction of nitrous acid, which is frequently present in commercial nitric acid, with o-phenylenediamine. The presence of the latter in the reaction mixture is due to the cleavage of the diazepine ring of the benzo-1,5-diazepine.

The main substance isolated from the mixture obtained was compound III. The structure of III was confirmed by the following facts, taken all together: the absence of a violet coloration in acid solutions of III, showing that the structure of a benzo-1,5-diazepine was not retained in III; the agreement of the elementary analysis and the molecular weight determined by mass spectrometry (M^+ m/e 237) with the empirical formula of III; the presence in the mass spectrum of III of peaks with m/e 195 and 153, due to the ejection of one and two CH_2CO molecules from the ion M^+, which is confirmed by the corresponding metastable peaks, and also of a peak with m/e 107 formed by the loss of a NO_2 group from the fragment with m/e 153; the showing up of the main structural elements of III in its IR spectrum by the usual frequencies (there are a broad band in the 3260-3285 cm^{-1} region, characteristic for the stretching vibrations of NH groups, and strong absorption of CO groups at 1660-1670 cm^{-1}); and the presence in the PMR spectrum of

Ordzhonikidze All-Union Scientific-Research Institute of Pharmaceutical Chemistry, Moscow.
Translated from Khimiya Geterotsiklicheskikh Soedinenii, Vol. 6, No. 8, pp. 1133-1134, August, 1970. Original article submitted January 3, 1969.

an isolated signal with δ 2.50 ppm corresponding to the six protons of two CH_3 groups and, in the weak-field region, the signals of three aromatic protons with δ 7.83, 8.33 and 8.43 ppm, interacting with one another with the characteristic ortho, meta and para constants, which shows the arrangment of the substituting groups in the benzene ring of III. Compound III was obtained independently by the acylation of 4-nitro-1,2-phenylenediamine.

EXPERIMENTAL

Action of a Mixture of Nitric and Sulfuric Acids on 2,4-Dimethylbenzo-1,5-diazepine. With stirring at 0-5°C, a mixture consisting of 6 ml of conc.H_2SO_4 and 4 ml of HNO_3 (d 1.43) was slowly added to a solution of 8.6 g (0.05 mole) of 2,4-dimethylbenzo-1,5-diazepine in 35 ml of conc.H_2SO_4. The reaction mixture was stirred at the same temperature for 1.5-2 hr and was poured onto ice. The resulting dark solution was neutralized with dry-ice cooling, and the oily substance that was liberated was immediately extracted with ethyl acetate. The extracts were dried with Na_2SO_4 and decolorized with activated carbon, and the solvent was evaporated off in vacuum. The dark oily residue (10.8 g) consisted of a mixture of substances decomposing even when heated in vacuum (1-2 mm). Substances I-III were isolated from the residue successively by repeated treatment with petroleum ether (bp 40°C), ether, and ethanol.

2-Acetyl-3-methylquinoxaline (I). Lustrous plates with mp 85-86.5°C [2]. Yield 2.4 g (26%).

Benzotriazole (II). Yield 0.48 g (8%). Mp 95-97°C (from ether), which corresponds to the figure given in the literature [3]. A mixture with an authentic sample of benzotriazole gave no depression of the melting point. Their UV and IR spectra were also completely identical.

N,N'-Diacetyl-4-nitro-1,2-phenylenediamine (III). The residue obtained after the successive treatment of 10.8 g of the mixture with petroleum ether and diethyl ether was boiled repeatedly with ethanol. The ethanolic solutions were combined and decolorized with carbon, and the ethanol was evaporated off. Yield 4.72 g (40%) of III. Mp 243.5-245°C. The melting point of a mixture of III and the N,N'-diacetyl-4-nitro-1,2-phenylenediamine obtained from 4-nitro-1,2-phenylenediamine and acetic anhydride showed no depression of the melting point.

The IR spectra were recorded on a UR-10 spectrophotometer in paraffin oil, the UV spectra on an EPS-3 recording spectrophotometer in ethanol, and the mass spectra on an MKh-1303 instrument fitted with a system for the introduction of the sample directly into the ion source close to the ionizing chamber at an ionizing voltage of ~30 V and a temperature of ~200°C (constancy of the temperature ±1°C).

The PMR spectra were taken on a JNM-4H-100 (100 MHz) instrument with TMS as internal standard and trifluoroacetic acid as solvent.

LITERATURE CITED

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