NEW METHOD FOR THE SYNTHESIS OF 2-(NITROMETHYL)BENZOXAZOLES

V. S. Grineva, V. A. Buevich,
and V. V. Rudchenko

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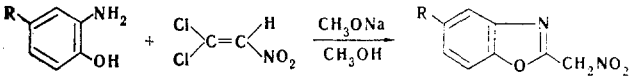
We propose a new method for the construction of the benzoxazole system by reaction of 1,1-dichloro-2-nitroethylene with o-aminophenol. Specifically, 1.1 g (0.01 mole) of o-aminophenol was dissolved in 20 ml of absolute methanol, and the solution was stirred at 10°C and poured into a solution of 1.42 g (0.01 mole) of 1,1-dichloro-2-nitroethylene in 10 ml of methanol. A solution of 0.46 g (0.02 g-atom) of sodium in 10 ml of methanol was then added dropwise in the course of 30 min. Sodium chloride began to precipitate after 5-10 min. The mixture was allowed to stand for 1 h, after which it was acidified with acetic acid and poured into ice water. The resulting yellow precipitate was removed by filtration and recrystallized twice from 70% aqueous methanol to give lemon-yellow needles of the known 2-(nitromethyl)benzoxazole (I), with mp 75°, in 57% yield. 5-Methyl-2-(nitromethyl)benzoxazole (II) was also obtained in 60% yield as lemon-yellow needles with mp 81° from 4-methyl-2-aminophenol. The results of a complete elementary analysis were in agreement with the calculated values.



I, II

I R=H; II R=CH$_3$

The reaction apparently proceeds through a step involving double nucleophilic addition to the double bond of 1,1-dichloro-2-nitroethylene and is facilitated by the formation, as a final product, of a five-membered ring with synchronous splitting out of the elements of hydrogen chloride in alkaline media. The bands at 1580 and 1350 cm^{-1} in the IR spectra of I and II are characteristic for a primary aliphatic nitro group.

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