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LETTERS TO THE EDITOR

Alkylation of 5-Amino-1,2,4-triazole with 1,2-Dibromoethane

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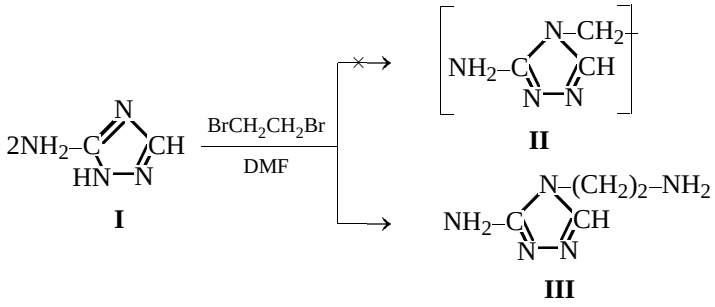
Azoles containing an NH pyridine nitrogen atom, along with a pyrrole group, can be alkylated under neutral conditions [1]. The reaction in this case is directed on the azo group and leads to formation of a quaternary salt which is treated with a base to isolate an *N*-substituted compound. Moreover, since aminotriazoles are relatively highly basic compounds capable of salt formation, then the role of the base can be played by excess heterocycle.

We expected that alkylation of 5-amino-1,2,4-triazole (**I**) with 1,2-dibromomethane (molar ratio 2 : 1) in DMF would give as major products isomeric bis(aminotriazolyl)ethanes like **II**.



I **II** **III**

However, the compound isolated from the reaction mixture had, according to the elemental analysis and ^{1}H NMR and IR spectra, had a structure different from the expected structure **II**.

It is known [1, 2] that alkylation of aminoazoles with haloalkanes in a neutral medium may give imines. In the imino form, the nucleophilic center is already the an exocyclic nitrogen atom, and alkylation here yields an alkylamino derivative.

Monoalkylation of triazole **I** can give rise to two through four isomers substituted by a ring nitrogen or by the amino group [3–6]. Cyclizations of compound **I** and its derivatives have been reported, involving the amino group and one of the ring nitrogens (N^2 or N^4) [7–11]. Depending on reaction conditions, one or two isomers in various ratios can be obtained.

Alkylation of triazole **I** with substituted bromoacetaldehydes in alkaline medium gave a mixture of isomers [12], two of which (N^1- and N^2-isomers) were then brought in cyclization by the amino group. The same reaction performed in the absence of base resulted in exclusive formation of the N^4-substituted isomer. Methylation of compound **I** in the absence of base, too, gave the N^4-isomer as the major product [13].

We alkylated triazole **I** with 1,2-dibromomethane at a molar ratio of 2 : 1 in DMF to obtain a compund whose elemental analysis and ^{1}H NMR and ^{13}C NMR and IR spectra suggested structure **III**.

5-Amino-4-(2-aminoethyl)-1,2,4-triazole. 1,2-Dibromomethane, 9.4 g, was added to a solution of 8.4 g of aminotriazole **I** in 50 ml of DMF. The reaction mixture was stirred at 85–90°C for 8 h and then cooled. The precipitate that formed was filtered off to isolate 4.01 g of compound **III**, yield 71%, mp 284–285°C (from methanol). IR spectrum, ν, cm^{-1}: 3245,

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3225, 1660 (NH), 1600, 1530, 1440, 1275, 1250, 1035, 980 (ring). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.10 s (4H, CH_2), 7.69 s (1H, CH), 11.50 br.s (1H, NH), 13.32 br.s (1N, NH). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 5.2 [2C, $(CH_2)_2$], 156.3 (2C, C_{arom}). Found, %: C 38.6; H 6.5; N 56.0. $C_4H_9N_5$. Calculated, %: C 38.1; H 6.3; N 55.6.

Thus, apparently, a rearrangement takes place, involving ring cleavage and nitrogen elimination, like the skeletal rearrangement of 3-chloro-4,5-diphenyl-4*H*-1,2,4-triazole, described in [14], with chlorine migration to the C^5 atom of the triazole ring, following nitrogen and benzonitirile elimination.

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