LETTER TO THE EDITOR

MESOIONIC 1,2,4-TRIAZOLO[5',1':3,4]-1,2,4-TRIAZOLO[1,5-a]-PYRIMIDINES

V. A. Chuiguk and I. A. Rudnik

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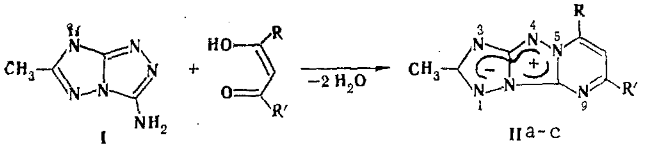
In the case of reactions of aminotriazolotriazole I with acetylacetone, benzoylacetone, and dibenzoylmethane we have shown that α-amino derivatives of nitrogen heterocycles whose molecules contain a "pyrrole" NH group that is remote from the amino group undergo condensation with 1,3-diketones to give mesoionic condensed pyrimidines with a common nitrogen atom, viz., triazolotriazolopyrimidines II in this case.



II a $R{=}R'{=}CH_3$; b $R{=}C_6H_5$, $R'{=}CH_3$; c $R{=}R'{=}C_6H_5$

Compounds II were formed by refluxing the components in trifluoroacetic acid for 2.5-3 h; dilution of the cooled reaction mixture with ether precipitated the trifluoroacetates of II, which, after recrystallization, were isolated in the form of bases II in 34, 40, and 41% yields with mp 190, 220-221, and 275°C, respectively. Compound IIa was also obtained by refluxing amine I in acetylacetone for 4 h. The PMR spectra of the compounds obtained were in agreement with their structures. The position of the substituents in IIb was determined from the character of the signal of the phenyl group in the PMR spectrum, in which the signal of the ortho protons is located 0.3 ppm away from the signals of the remaining protons of the phenyl group [1]. Heterocyclic system II was previously obtained in the form of 2,3-diamino derivatives of the cations [2].

Bases II are colorless (IIa), yellowish (IIb), or yellow (IIc) substances; this is in agreement with their UV spectra [λ_{max} ($\varepsilon \cdot 10^{-3}$)] (in methanol): IIa 260 (5.02), IIb 243 (9.32), 270 (19.90), 322 (3.65), 378 (3.24); IIc 243 (8.4), 297 (25.80), 398 nm (5.96). They form both protic and quaternary salts. Thus the perchlorate of base IIa (mp 294-295°C) was obtained by the action of perchloric acid, while the methylperchlorates (mp 178-179 and 301-302°C, respectively) were obtained by heating IIa, c with methyl p-tosylate (at 140-150°C for 1 h) with subsequent treatment with perchloric acid. The PMR spectra of the quaternary salts make it possible to exclude alkylation at the N_4 atom; alkylation probably takes place at the most basic N_3 atom. Both the protic and quaternary salts of bases IIa, b (in contrast to the salts of base IIc) give methylidyne dyes due to the activity of the methyl group in the 8 position. The relatively small difference in the color of the p-dimethylaminostyryl base from perchlorate IIa (λ_{max} 463 nm) and the color of the dye salt (λ_{max} 490 nm) correspond to a mesoionic structure for II and their derivatives. Base IIb and the methylperchlorates were recrystallized from methanol, base IIa was recrystallized from acetone, its perchlorate was recrystallized from ethanol, and IIc was recrystallized from dimethylformamide. The results of elementary analysis of the compounds obtained were in agreement with the calculated values.

LITERATURE CITED

1. M. K. Pordeli, V. V. Oksanich, and V. A. Chuiguk, Khim. Geterotsikl. Soedin., No. 10, 1285 (1973).
2. V. A. Chuiguk and K. V. Fedotov, Ukr. Khim. Zh., 46, No. 9, 1092 (1980).

T. G. Shevchenko Kiev State University, Kiev 252017. Translated from Khimiya Geterotsiklicheskik Soedinenii, No. 7, p. 993, July, 1982. Original article submitted December 2, 1981.

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