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THE NITROGEN-NITROGEN BOND CLEAVAGE OF 1,3,4-THIADIAZOLO-[3,2-a]PYRIMIDINES TO 2-THIOCYANATOPYRIMIDINES

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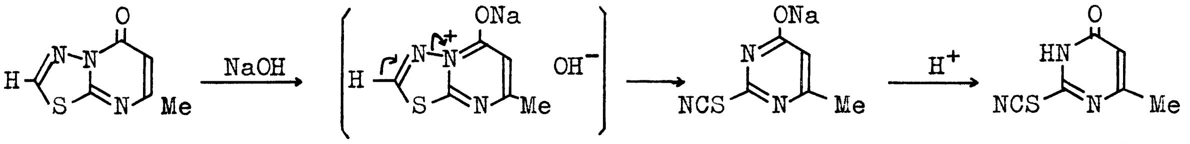
Treatment of 7-methyl-5H-1,3,4-thiadiazolo[3,2-a]pyrimidin-5-one with aq. NaOH solution gave 4-methyl-2-thiocyanato-6(1H)-pyrimidone. In a similar manner, two thiadiazolopyrimidines prepared by the Vilsmeier-Haack reaction of 1,4,6-triamino-2(1H)-pyrimidinethione, were converted into 2-thiocyanatopyrimidines.

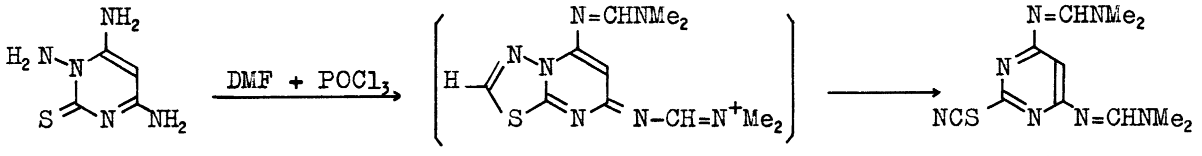
Two research groups[1,2] have reported the synthesis of 1,3,4-thiadiazolo-[3,2-a]pyrimidines. However, there seems to be no literature concerning their reactivity. The present paper describes the nitrogen-nitrogen bond cleavage of 1,3,4-thiadiazolo[3,2-a]pyrimidines to give 2-thiocyanatopyrimidines.

Reaction of 7-methyl-5H-1,3,4-thiadiazolo[3,2-a]pyrimidin-5-one (I, prepared from 3-amino-6-methyl-4(3H)-oxo-2(1H)-pyrimidinethione[2]) with an excess amount of 5 % NaOH solution at room temperature for 1 hr afforded 4-methyl-2-thiocyanato-6(1H)-pyrimidone (III), mp 168-169°; IR λ_{max}^{KBr} 2175 cm^{-1} (-SCN). The structure was confirmed by the elementary analysis and by comparison with the authentic sample prepared from 6-methyl-2-thiouracil and cyanogen bromide. Since the conversion of (I) into (III) did not occur by aq. Na_2CO_3 solution, it seems plausible that the formation of (III) depended on the strength of the base, and so on.



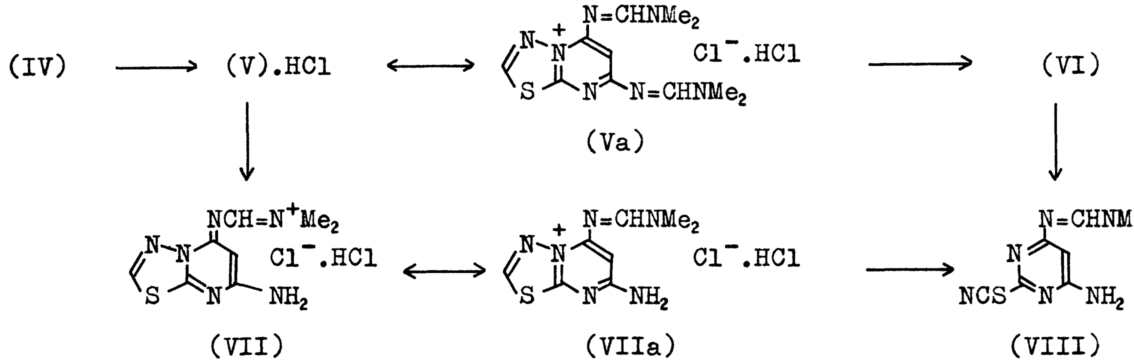
(I) (II) (III)

This finding led us to conceive an idea to reexamine the Vilsmeier-Haack reaction of 1,4,6-triamino-2(1H)-pyrimidinethione (IV), which was reported by Taylor and Morrison[3] relating the proposed mechanism involving the formation of thiadiazolopyrimidine (V) as the intermediate, followed by its self-decomposition into 4,6-bis-(dimethylaminomethylenamino)-2-thiocyanatopyrimidine (VI). By the reexamination,

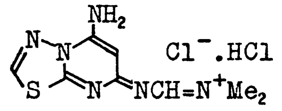


(IV) (V) (VI)

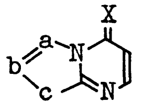
we obtained two thiadiazolopyrimidines (V) and (VII), which were converted into 2-thiocyanatopyrimidines upon treatment with aq. NaOH solution. In the Taylors' procedure, the precipitate deposited in the reaction mixture was not characterized, but immediately treated with NaOH to isolate (VI). In the present experiment, the precipitate was washed with a small amount of ice-water prior to the alkaline treatment. In the IR spectrum (KBr), the crude material showed the $C=N^+$ absorption at 1710 cm^{-1} in the absence of the -SCN absorption. Thus, the structure of the precipitate was assumed to be the hydrochloride of (V). Dissolution of the substance into aq. NaOH solution afforded (VI). Recrystallization of the precipitate from H_2O resulted the hydrolysis of the dimethylaminomethylenamino group to give (VII), mp 134-136°; corresponding the elementary analysis with $C_8H_{12}N_6SCl_2 \cdot 2H_2O$. IR λ_{max}^{KBr} 3000 (NH_3^+), 1710 cm^{-1} ($C=N^+$). UV $\lambda_{max}^{H_2O}$ (ε) 247(22800), 270(14400), 303(22400), 327 nm(38400). Therefore, the structure of (VII) was deduced as 7-amino-5-dimethylaminomethylenaminothiadiazolo[3,2-a]pyrimidinium



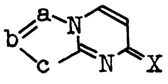
chloride. The possibility of the alternative structure (VIIb) was excluded judging from the ratio of the extinction coefficient of the absorption at 327 nm to that of the absorption at 270 nm. The value was 2.7, which was consistent with the structure of polyazaindene (IX), but not (X).1) Since the facile formation of 4-amino-6-dimethylaminomethylenamino-2-thiocyanatopyrimidine (VIII) from (VI) with HCl is known,3) it is likely that the hydrolysis of the hydrochloride of (V) into (VII) took place during the recrystallization. Treatment of (VII) with NaOH gave (VIII) identical in all respects with the authentic sample.3)



(VIIb)



(IX)



(X)

In conclusion, it is pointed out that 1,3,4-thiadiazolo[3,2-a]pyrimidines having the possibility to form such a thiadiazolopyrimidinium structure as (II), (Va) or (VIIa), could be converted into 2-thiocyanatopyrimidines upon treatment with aq. NaOH solution.

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