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SYNTHESIS AND PROPERTIES OF ANALOGS OF 5(4)-AMINOIMIDAZOLE-4(5)-CARBOXAMIDE AND PURINES.

15.* RING OPENING IN IMIDAZO[4,5-d]-1,2,3-TRIAZINES

V. K. Usova, I. S. Selezneva,
T. A. Pospelova, and V. S. Mokrushin

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It has been shown that 4-methylthio-, ethoxy-, and methoxyimidazotriazines and imidazotriazin-4-ones, unlike benzo-1,2,3-triazines, do not display cryptodiazonium behavior. A novel type of fission of the triazine ring to give esters and thioesters of 5-aminoimidazole-4-carboxylic acid is described.

It is known that imidazotri- and -tetrazoles and -triazines [2-4], like benzotriazines [5], undergo cleavage of the triazine ring in acid media or on treatment with nucleophiles to give diazo-compounds. We report here some aspects of the behavior of 4-chloro-, thio-, and alkoxyimidazotriazines (Ia-d) in aqueous acid media.

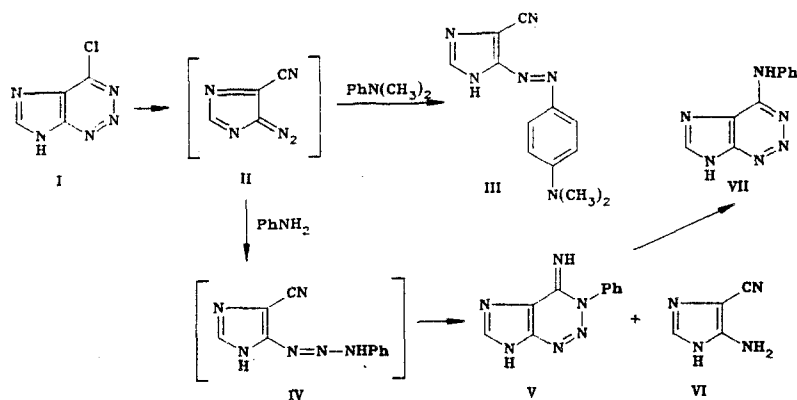
On heating the chloroimidotriazine (Ia) with dimethylaniline in aqueous hydrochloric acid, there was obtained the expected imidazole (III), identical (IR and UV spectra) with that reported previously [3].

With aniline, on the other hand, N- rather than C-azocoupling of 5-diazoimidazole-4-carbonitrile (II), formed by fission of the N₍₂₎-N₍₃₎ bond in the triazine ring in (Ia), takes place. The resulting monosubstituted triazine (IV), like 5-(3-methyl-1-triazeno)-imidazole-4-carbonitrile [3], is then converted under the reaction conditions into the 4-iminotriazine (V). (Formula, top, following page.)

Confirmation of this reaction scheme was provided by the isolation from the reaction mixture of the aminoimidazolecarbonitrile (VI), and by the formation of (V) directly from the diazimidazole (II) and aniline [3].

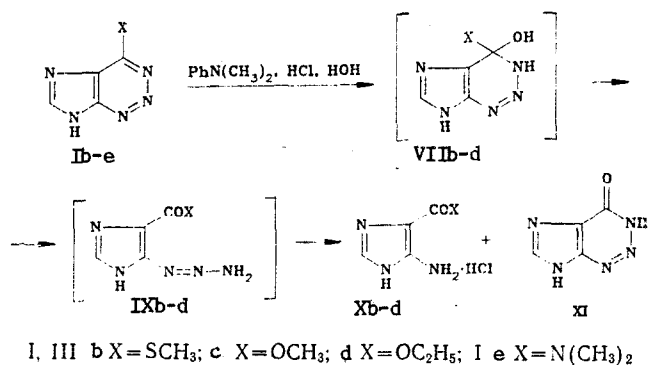
For Communication 14, see [1].

S. M. Kirov Urals Polytechnic Institute, Sverdlovsk 620002. Translated from *Khimiya Geterotsiklicheskih Soedinenii*, No. 9, pp. 1248-1250, September, 1989. Original article submitted September 18, 1987; revision submitted December 19, 1988.



The iminotriazine (V), like 4-imino-3-methylimidazotriazine and the corresponding benzotriazine [3, 6], undergoes a Dimroth rearrangement on heating in water to give the phenylamino-triazine (VII).

It might be expected that the triazine ring in (Ib-e) would also be cleaved by fission of the $\text{N}_{(2)}-\text{N}_{(3)}$ bond in acid media. However, on heating (Ib-e) in hydrochloric acid, either with or without the addition of dimethylaniline, azo-compounds were not detected, even by thin-layer chromatography. There were isolated from the reaction mixture the previously-reported amino-imidazoles (Xb-d) [7-9] and around 5% of the azahypoxanthine (XI).



The absence of azo-coupling, even in the presence of dimethylaniline, which is an efficient trap for diazo-compounds, totally excludes rupture of the $\text{N}_{(2)}-\text{N}_{(3)}$ bond in triazines (Ib-d) [10].

This striking difference in the behavior of imidotriazines (Ib-e) and (Ia) could be due to the fact that the chlorine in (Ia) is a good cleaving group, whereas cleavage of the methylthio, dimethylamino-, and alkoxy-groups in (Ib-e) is more difficult.

The triazenes (IXb-d) formed by aza-transfer undergo cleavage to the aminoimidazoles (Xb-d), and cyclize partially to the azahypoxanthine (XI). This cleavage of the triazine ring at $\text{C}_{(4)}-\text{N}_{(3)}$ has not been reported previously in condensed 1,2,3-triazines with a substituent in the 4-position.

Attempts to cleave the triazine ring in the azahypoxanthine (XI) and the dimethylamino-triazine (Ie) by heating in hydrochloric acid, and also in the presence of dimethylaniline or copper(I) chloride, were unsuccessful. Hence, compounds (XI) and (Ie), unlike the benzoderivatives of similar structure, show no cryptodiazonium properties.

EXPERIMENTAL

IR spectra were obtained on a UR-20 in KBr disks, and UV spectra on a Beckman UV-26 spectrophotometer, in ethanol. PMR spectra were recorded on a Perkin-Elmer 12B (60 MHz) in DMSO-D_6 , internal standard TMS. Chromatography was carried out on Silufol UV-254 plates in the systems: n-propanol-0.2 N ammonia, 3:1 (R_{f1}); N-butanol-acetic acid-water-ethyl acetate, 4:1:1:1 (R_{f2}); and chloroform-ethanol, 9:1 (R_{f3}). The chromatograms were treated with a solu-

tion of m-phenylenediamine in ethanol, diazo-compounds giving a strong coloration, and imidotriazines developing a color on heating. The elemental analyses of the products were in agreement with the calculated values.

5-(4-N,N-Dimethylaminophenylazo)imidazole-4-carbonitrile (III, C₁₂H₁₂N₆·HCl). A mixture of 0.1 g (0.58 mmole) of the triazine (Ia) in 3 ml of 2 N aqueous HCl and 0.07 ml (0.70 mmole) of dimethylaniline was heated to boiling, cooled, and a saturated solution of sodium acetate added to pH 6. The solid which separated was filtered off, washed with water, and dried in a vacuum desiccator over P₂O₅, to give 0.10 g (63%) of product, mp 230-231°C, R_{f1} 0.87, R_{f3} 0.60. IR spectrum: 2240 cm⁻¹ (C≡N). UV spectrum, λ_{max} (log ε): 275 (3.84), 480 nm (4.55).

4-Imino-3-phenylimidazo[4,5-d]-1,2,3-triazine (V, C₁₀H₈N₆), and 5-Aminomidazole-4-carbonitrile (VI). A. To a solution of 0.17 g (0.98 mmole) of the triazine (Ia) in 7 ml of ethanol was added 2.04 ml (22 mmole) of aniline, and the mixture kept at room temperature for three days. The solid which separated was filtered off, and crystallized from ethanol, to give 0.14 g (67%) of the imine (V), mp 260°C, R_{f1} 0.51; R_{f2} 0.52; R_{f3} 0.49. UV spectrum, λ_{max} (log ε): 205 (3.98), 230 (3.75), 285 (3.86), 380 nm (3.20). PMR spectrum 8.63 (1H, s, CH); 7.40 ppm (5H, m, Ph).

B. To a solution of 0.20 g (1.68 mmole) of the diazoimidazole (II) in 50 ml of chloroform was added dropwise at 5°C 0.17 ml (1.83 mmole) of aniline. The mixture was stirred for 2 h, and the solid filtered off and crystallized from ethanol to give 0.18 g (51%) of (V). The UV spectrum and mp of the product were identical with those described in method A. The ethanolic filtrate was evaporated under reduced pressure, and the residue dissolved in 15 ml of ethanol, boiled for 20 min with activated charcoal, and filtered. The filtrate was evaporated to dryness under reduced pressure, and triturated with ether, to give 0.02 g (12%) of (VI), identical in its physicochemical properties with a sample obtained as in [10].

4-Phenylaminoimidazo[4,5-d]-1,2,3-triazine (VII, C₁₀H₈N₆). A suspension of 0.4 g (2.0 mmole) of (V) in 20 ml of water was boiled for 30 min, cooled, and the solid filtered off and crystallized from water, to give 0.3 g (75%) of product, mp 240°C. R_{f1} 0.27; R_{f2} 0.60; R_{f3} 0.18. UV spectrum, λ_{max} (log ε): 210 (3.94), 232 (4.00), 280 nm (3.15).

Methyl 5-Aminoimidazole-4-thiocarboxylate (Xb). A solution of 10 mmole of the triazine (Ib) in 30 ml of aqueous hydrochloric acid was boiled for 2 h, evaporated to dryness under reduced pressure, and the residue crystallized from ethanol, to give 1.67 g (86%) of (Xb) hydrochloride, the IR and UV spectra of which were identical with those reported previously [9]. Obtained similarly were (Xc, d) [7, 8]. The presence and amount of azahypoxanthine were determined semiquantitatively by TLC in comparison with an authentic sample [11].

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