

SYNTHESIS OF NITRO-, NITROSO-, AND AZOXY-1,3,5-  
TRIAZINES BY THE OXIDATION OF 2-HYDROXYAMINO-4,6-  
BIS(DIMETHYLAMINO)-1,3,5-TRIAZINE

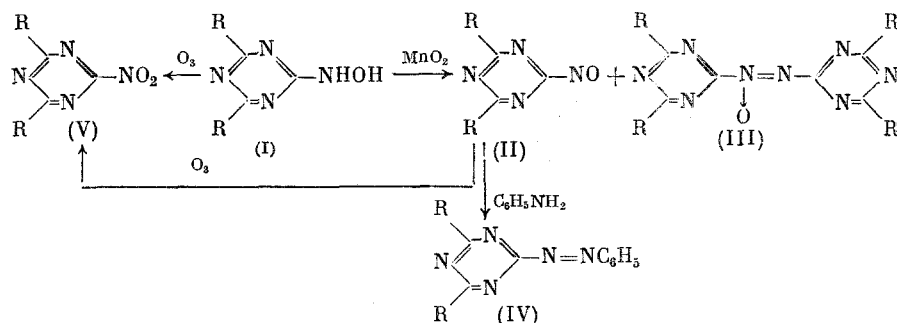
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1,3,5-Triazine derivatives with electron-withdrawing ring substituents such as nitro, nitroso and azoxy groups were unknown until recently [1]. Stable substituted 2-nitro-1,3,5-triazines have now been obtained for the first time by the photooxidation of azido-1,3,5-triazines [2].

We have shown that 2-hydroxyamino-4,6-bis(dimethylamino)-1,3,5-triazine (I), which was obtained in 60% yield by the reaction of the corresponding 2-chlorotriazine with hydroxylamine according to Matsui et al. [3], oxidizes by the effect of activated  $\text{MnO}_2$  in chloroform at 20°C to form the first representatives of nitroso and azoxy derivatives of 1,3,5-triazine, namely, 2-nitroso-4,6-bis(dimethylamino)- (II) and 4,4',6,6'-tetrakis-(dimethylamino)-2,2'-azoxy-1,3,5-triazines (III). The structure of (II) was confirmed by the preparation of 2-phenylazo-4,6-bis(dimethylamino)-1,3,5-triazine (IV).

The oxidation of (I) or (II) by ozone in chloroform at 0-5°C led to 2-nitro-4,6-bis-(dimethylamino)-1,3,5-triazine (V) identical to that described in our previous work [2]. The isolation of (V) was carried out by thin-layer chromatography on Silufol plates with 98:2 chloroform-acetone as eluant



$\text{R} = \text{N}(\text{CH}_3)_2$ .

Product (II) was obtained in 35% yield, mp 171-174°C (dec., from ethyl acetate). Product (III) was obtained in 35% yield; mp 243-245°C (from ethyl acetate), mol. wt. 376.2193 (high-resolution mass spectrometry). Product (IV) was obtained in 74% yield, mp 114-115°C (from petroleum ether), mol. wt. 271.1524 (high-resolution mass spectrometry). Product (V):  $\text{M}^+$  212.1018,  $(\text{M} - \text{NO}_2)^+$  166.1085; this product was obtained in 28% yield from (I) and 50% yield from (II), mp 124-126°C.

The structures of these compounds were supported by elemental analysis data and IR and PMR spectroscopy. The behavior of other hydroxyamino-1,3,5-triazines upon the action of oxidizing agents is under study.

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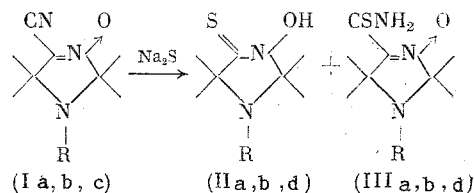
TRANSFORMATION OF 4-CYANO-2,2,5,5-TETRAMETHYL-  
3-IMIDAZOLINE 3-OXIDES (CYCLIC  $\alpha$ -CYANONITRONES)  
INTO THIOHYDROXAMIC ACIDS

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4-Cyano-2,2,5,5-tetramethyl-2-imidazoline 3-oxides (Ia)-(Ic) react with O-nucleophiles depending on the conditions to give either products of addition at the cyano group or products of the replacement of this group [1]. In light of the interest in thiohydroxamic acids and the limited pathways for their synthesis [2], we examined the possibility of obtaining thiohydroxamic acids by the replacement of the cyano group in (Ia)-(Ic).

The treatment of (Ia)-(Ic) by ethanolic KSH or  $\text{Na}_2\text{S}$  at about  $20^\circ\text{C}$  gives thiohydroxamic acids (IIa) and (IIb) and thioamides (IIIa) and (IIIb). In the case of paramagnetic derivative (Ic), we also encounter the reduction of the nitroxyl group to an amino group, which leads to (IIId) and (IIIId).



R =  $\text{CH}_3$  (a), NO (b), O $\cdot$  (c), H (d).

The structures of (IIa), (IIb), (IIId), (IIIa), (IIIb), and (IIIId) were indicated by spectral and analytical data. Product (IIa) was obtained in 85% yield, mp  $100-103^\circ\text{C}$  (from ethanol). Product (IIId) was obtained in 70% yield, mp  $134-136^\circ\text{C}$  (from ethanol). Product (IIIa) was obtained in 14% yield, mp  $144-145^\circ\text{C}$  (from methanol). Product (IIIb) was obtained in trace amounts, mp  $180-183^\circ\text{C}$  (from ethanol). Product (IIIId) was obtained in 15% yield, mp  $163^\circ\text{C}$  (dec.) (from ethanol).

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