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On Products of Nitration of bis-4,4'-(Dimethylamine)-azoxybenzene

by

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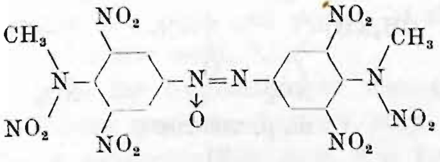
Continuing our experiments on nitration of derivatives of azoxybenzene [1], [2], we nitrated *bis*-4, 4'-(dimethylamine)-azoxybenzene *) to yield a hexanitroazoxyderivative. We assumed its structure to be of an "azoxytetryl" (I), by analogy to the well known nitration of dimethylaniline to tetryl.

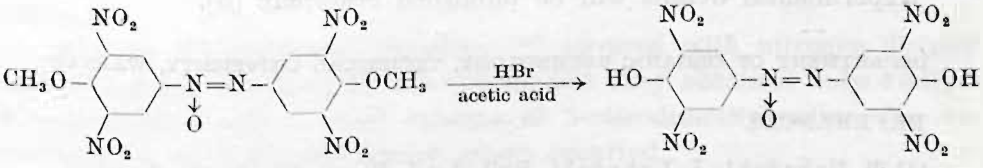
We tried to prove the structure of (I) by hydrolizing the methylnitramine groups to phenolic ones. However, boiling of (I) with concentrated (10-40%) solution of sodium or potassium carbonate, or diluted (0.5-5%) solution of sodium or potassium hydroxide did not furnish any crystalline product.



m. p. 208–209°C. (decomp.)

(I)

Therefore another way of confirming the structure of (I) was chosen. It consisted in synthesizing (I), from the tetranitroazoxyanisole [1] previously described [1], by the following sequence of reactions:



m. p. 186–187°C.

(II)

(III)

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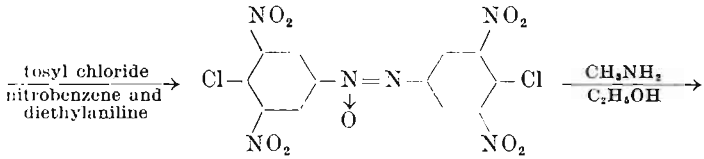
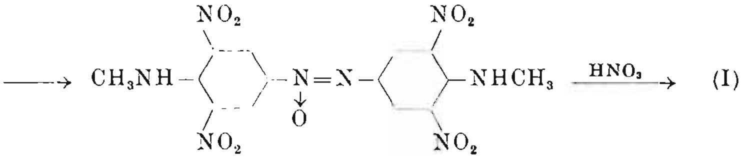
*) We prepared this compound from *p*-nitrosodimethylaniline by an improved method which will be described elsewhere [3].

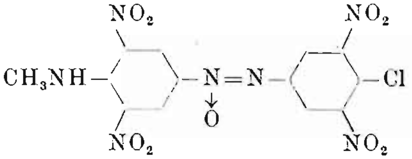


m. p. 226-228°C.
(IV)



m. p. 260-261°C. (decomp.)
(V)

In the course of experiments on the transformation of (IV) into (V), we noticed that, when methylamine in toluene medium was used, only partial substitution of chlorine by the methylamine group occurred and yielded an unsymmetrical compound. Taking into consideration that chlorine attached to the "B ring" is more mobile than the other one (according to Angeli's theory [4]), we ascribed the structure (VI) to this compound. The formation of this unsymmetrical compound can be taken as an additional proof of the unsymmetrical structure of the azoxy group.



m. p. 206-208°C.
VI

We also tried to prepare compound (V) directly from (II) by heating it with methylamine in toluene solution at 130-140°. The reaction led only partially to the formation of (V), the main product being (III), evidently resulting from hydrolysis of (II).

Experimental details will be published elsewhere [5].

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[1] T. Urbański, J. Urbański, Bull. Acad. Polon. Sci., in this issue.
[2] — Bull. Acad. Polon. Sci., in this issue.
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[4] A. Angeli, *Über die Konstitution der Azoxyverbindungen*, Stuttgart, 1913; Gazz. chim. ital. **46**, II (1916), 67.
[5] T. Urbański, J. Urbański, Roczniki Chem. (in press).