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On Products of Nitration of *p, p'*-Azoxyanisole

by

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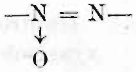
Strong evidence was given by Angeli [1], [2], that the azoxy group in aromatic compounds possesses an asymmetric structure, viz.



$$-\underset{\substack{\downarrow\\ \text{O}}}{\text{N}}=\text{N}-$$

A few authors confirmed it, e. g. Behr [3].

To facilitate further description we suggest to denote two aromatic rings: *A* and *B*.

The ring nearest to the $-\underset{\substack{\downarrow\\ \text{O}}}{\text{N}}=$ moiety of the azoxy group would be called "*B* ring" (diagram, Fig. 1)

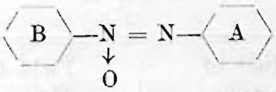


Fig. 1

The substituents of "*B* ring" would bear customary notion *o'*, *m'*, *p'* or 2', 3', 4' [3].

However, it seems desirable to collect a still wider experimental evidence supporting the theory of Angeli.

We have chosen reaction of nitration of *p, p'*-azoxyanisole ((I) Table C) expecting that substitution of both aromatic rings of this compound will be different, similarly to the nitration of azoxybenzene [4]-[7] and its various derivatives [8]-[11] to corresponding mono- and trinitro-azoxycompounds. It is important to note that the "*B*-benzene ring" was never in these experiments nitrated to more than one nitro group.

We started by nitrating *p, p'*-azoxyanisole with ordinary nitrating mixtures composed of nitric and sulphuric acid. This however did not furnish good results, the products being impure.

Also nitration with nitric acid (*d* 1.50) gave similar results.

More uniform results and good yields were obtained on nitration of (I) with nitric acid of lower concentration (70-85% HNO_3).

Depending on conditions of the reaction, dinitro- (II), trinitro- (III) and tetranitroazoxyanisole (IV) resulted. Good results were also obtained, when azoxyanisole was nitrated with a mixture of nitric and acetic acid (Table I):

TABLE I

Nitrating mixture	Temperature of nitration	Product of nitration	Yield (% of theoretical)	m. p. °C.
40% HNO_3 55% CH_3COOH 5% H_2O	20	dinitroazoxyanisole (II)	60	210–212°
64% HNO_3 34% CH_3COOH 2% H_2O	85°	trinitroazoxyanisole (III)	60	179–180°

The best results were obtained when azoxyanisole was nitrated with a mixture of nitric acid (*d* 1.50) with phosphoric acid (85%) (ratio $\frac{50}{50}$ by weight) – Table II.

TABLE II

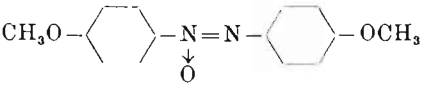
Temperature of nitration	Product of nitration	Yield (% of theoretical)	m. p. °C.
30°	trinitroazoxyanisole (III)	80	179–180°
50°	,,	70	179–180°
80°	tetranitroazoxyanisole (IV)	35	239–240°

Nitration of azoxyanisole with mixtures of anhydrous nitric and phosphoric acids furnished tetranitroazoxyanisole (IV) with a smaller yield.

It is evident that introduction of three nitro groups into a molecule of azoxyanisole occurred with relative ease. But the introduction of the fourth nitro group required more drastic reaction conditions.

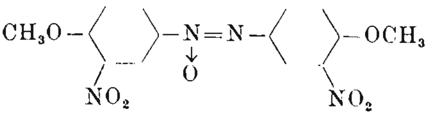
It constitutes an additional proof of the fact that the "*B*-benzene ring" is less readily nitrated than the "*A*-ring".

TABLE III



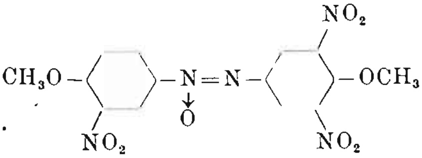
m. p. 116°

(I)



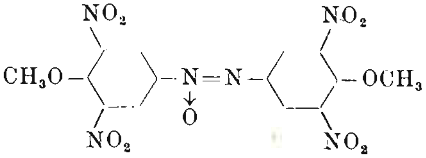
m. p. 210-212°

(II)



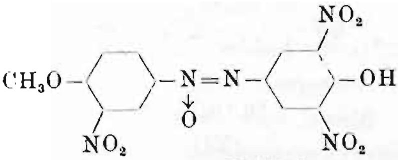
m. p. 179-180°

(III)



m. p. 239-240°

(IV)

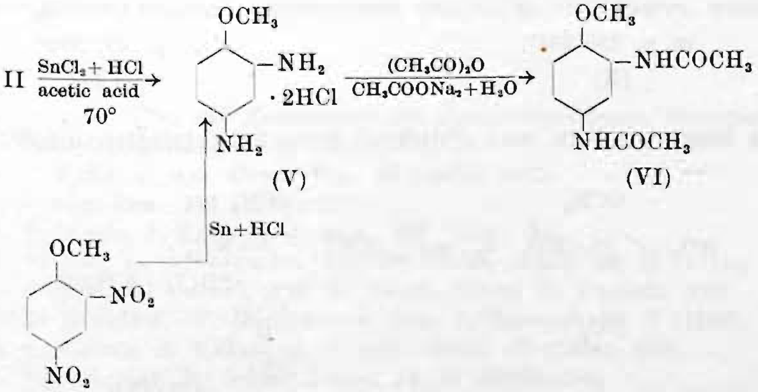


m. p. 179-181°

(XII)

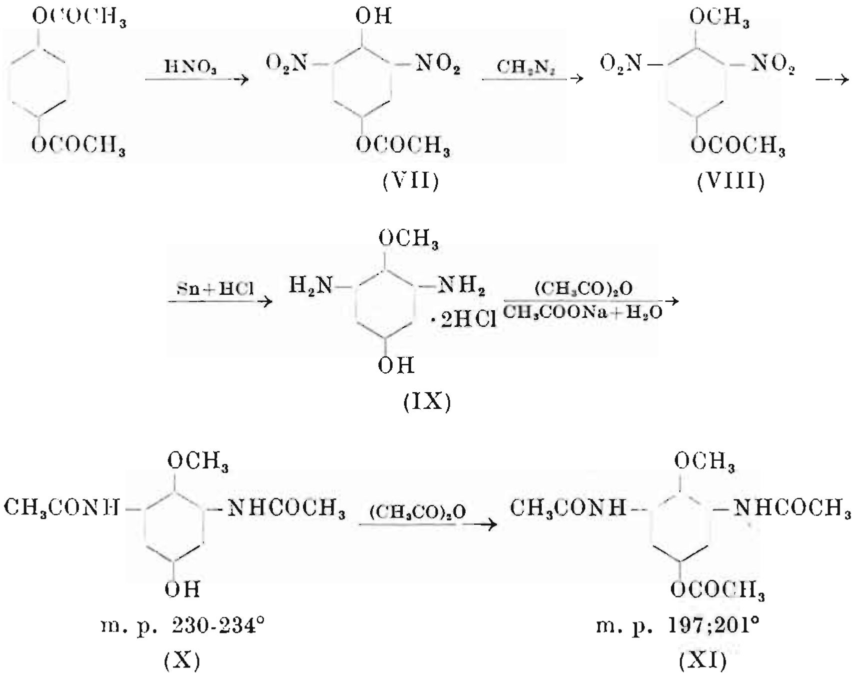
Structure of the products of nitration of anoxyanisole

Dinitroazoxyanisole (II). The structure was determined by reduction of (II) with stannous chloride and hydrochloric acid in the presence of acetic acid. Dihydrochloride of 2,4-diaminoanisole (V) resulted. The same compound was prepared from 2,4-dinitroanisole. The diamino-compound (V) prepared in both ways was converted into N-diacetyl derivative (VI):

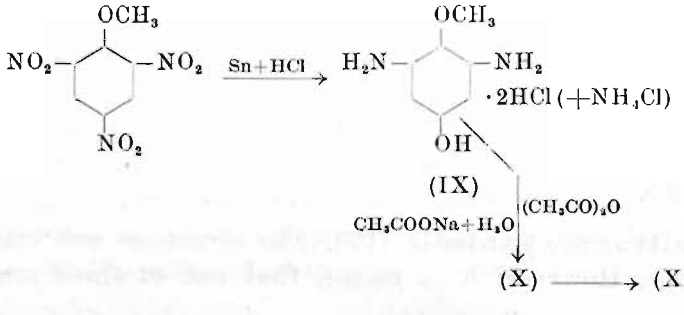


Tetranitroazoxyanisole (IV). The structure was established in a similar way. However, it is known that one of three amino groups formed during the reduction of trinitroanisole is readily hydrolised to phenolic group [12]. We noticed the same fact on reduction of (IV) — the same diaminohydroxyanisole resulted. The position of the phenolic group in this compound remained so far unknown and it was necessary to begin with a determination of the structure of diaminohydroxyanisole.

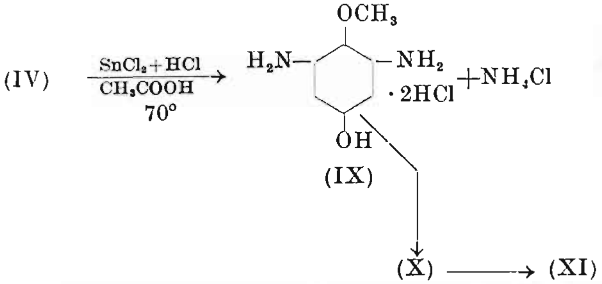
This was done by the following sequence of reactions. Quinol was acetylated and nitrated to known 4-acetoxy-2,6-dinitrophenol (VII). This was converted to methyl ether (VIII) by acting with diazomethane. Reduction of (VIII) with tin and hydrochloric acid was accompanied by hydrolysis of the O-acetyl group (IX). Acetylation of this compound in aqueous medium yielded N-diacetyl derivative (X). This was acetylated in anhydrous medium to yield the final product — 2,6-diacetylamino-4-acetoxyanisole (XI):



The same product was obtained from 2,4,6-trinitroanisole:



Also, when tetranitroazoxyanisole (IV) was reduced with stannous chloride and hydrochloric acid, hydrochloride of the compound (IX) and ammonium chloride resulted:



This was further acetylated stepwise (as described above) to yield (X), and finally (XI).

Trinitroazoxyanisole (III)

Reduction of trinitroazoxyanisole yielded a mixture of partly resinified products. It was difficult to isolate the components in pure forms. Only a small quantity of 2,4-diaminoanisole was found. Therefore we limited ourselves to nitration of (III) to tetranitroderivative. The latter was identical with the product (IV), thus the substitution of the two benzene rings is 3,5 and 3' respectively. On the basis of Angeli's theory it should be admitted that the lower nitrated benzene ring is neared to $\underset{\|}{\overset{|}{N}}\rightarrow O$ moiety of the azoxy group, i. e. the structure is (III).

The lack of symmetry of compound (III) produces different mobility of methoxy groups. Thus, on hydrolysis with hydrobromic acid in presence of acetic acid, 4-hydroxy-4'-methoxy-3, 5, 3'-trinitroazoxybenzene (XII) resulted.

Experimental details of this work will be published elsewhere [13].

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