Mechanisms of the Wallach Rearrangement

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Shemyakin, Maimind and Vaichunaite$^{1)}$ have shown, using ^{15}N-labeled azoxybenzene (I) that I was observed to rearrange to 4-hydroxyazobenzene (III) or (IV) under various conditions$^{2,3)}$

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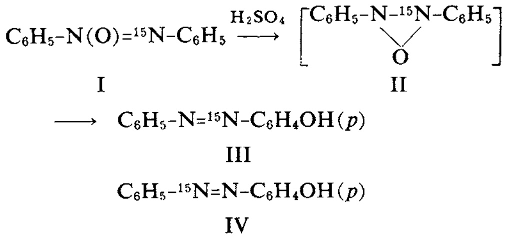
1) M. M. Shemyakin, V. J. Maimind and B. K. Vaichunaite, *Chem. & Ind.*, **1958**, 755; Izvestia Akad. *Nauk S. S. S. R., Otdel. Khim. Nauk*, 866 (1960).

2) P. H. Gore and G. K. Hughes, *Austral. J. Sci. Research*, **3A**, 136 (1950); *Chem. Abstr.*, **45**, 2889 (1951).

3) V. O. Lukashwish and T. N. Khurdyumova, *Zhur. Obshchei Khim.*, **18**, 1961 (1948).

in which the two benzene rings were attacked with equal ease. Azoxybenzene recovered from these reactions remained practically unchanged in isotope distribution: They postulated that the rearrangement proceeds through a symmetrical intermediate, II.

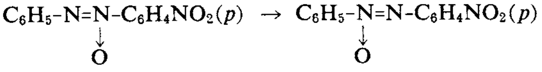


$$C_6H_5\text{-}N(O)\text{=}^{15}N\text{-}C_6H_5 \xrightarrow{H_2SO_4} \left[C_6H_5\text{-}N\text{-}^{15}N\text{-}C_6H_5\right] \longrightarrow C_6H_5\text{-}N\text{=}^{15}N\text{-}C_6H_4OH(p)$$

$$C_6H_5\text{-}^{15}N\text{=}N\text{-}C_6H_4OH(p)$$

I II III IV

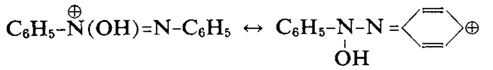
The formation of the *N*, *N*-oxide intermediate II was further emphasized by the Russian workers[4] in their finding that there was no incorporation of ^{18}O into *p*-nitroazoxybenzene from ^{18}O-labeled sulfuric acid in the isomerization of *β*-*p*-nitroazoxybenzene (V) to *α*-*p*-nitroazoxybenzene (VI).



$$C_6H_5\text{-}\underset{\downarrow\atop O}{N}\text{=}N\text{-}C_6H_4NO_2(p) \rightarrow C_6H_5\text{-}N\text{=}\underset{\downarrow\atop O}{N}\text{-}C_6H_4NO_2(p)$$

V VI

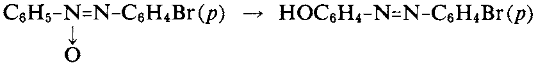
An alternative mechanism was suggested by Gore[5] to proceed via monocation (VII) in which nucleophilic attack by $-OSO_2OH$ or $-OSO_2Cl$ is restricted to the far ring.



$$C_6H_5\text{-}\overset{\oplus}{N}(OH)\text{=}N\text{-}C_6H_5 \leftrightarrow C_6H_5\text{-}\underset{OH}{N}\text{-}N\text{=}C_6H_5^{\oplus}$$

VII

The latter mechanism is similar to that of the Bamberger reaction[6] and one can expect that the *p*-positions would be attacked preferentially by more nucleophilic ethoxy group when the reaction is conducted in the mixture of ethanol-sulfuric acid as was shown by Yukawa[7], in the case of the Bamberger reaction. *p*-Aminophenol formed by the Bamberger reaction of phenylhydroxylamine was shown to incorporate ^{18}O from the reaction medium when the reaction was carried out in ^{18}O-labeled sulfuric acid[8]. We have carried out the reaction by heating azoxybenzene in the mixture of ethanol and sulfuric acid for 5 hr. at 90°C, but the reaction was found to proceed very little, recovering original material in almost quantitative yield. We have reacted azoxybenzene in 83% sulfuric acid, labeled by 0.67% ^{18}O and found that the resulting *p*-hydroxyazobenzene incorporated no ^{18}O from the medium (CO_2 found, 0.202 ^{18}O, tank CO_2, 0.204% ^{18}O). We also found that the rearrangement of *α*-*p*-bromoazoxybenzene was much slower than that of unsubstituted compound in the same medium (83% H_2SO_4).



$$\underset{\downarrow\atop O}{C_6H_5\text{-}N}\text{=}N\text{-}C_6H_4Br(p) \rightarrow HOC_6H_4\text{-}N\text{=}N\text{-}C_6H_4Br(p)$$

VIII IX

α-*p*-Nitroazoxybenzene is known to rearrange slowly[5]. These findings together with the fact that a substantial proportion of azoxybenzene is reduced by potassium iodide to azobenzene in the rearrangement reaction in chlorosulfonic acid, seem to suggest that the rearrangement in these oxy-acids is an acid catalyzed bimolecular oxidation reaction where *p*-positions of benzene rings of the *N*, *N*-oxide II or of azoxybenzene are attacked by oxygen of protonated *N*, *N*-oxide II or *N*-oxide.

A similar rearrangement of azoxybenzene to *o*-hydroxyazobenzene by ultraviolet light has been known[9]. In this case, the reaction take place not only in non-acidic medium, such as aqueous alcohol but also in solid state. The Russian workers[1] found that the original excess of ^{15}N was in the nitrogen group attached to the hydroxylated benzene when carried out the reaction in 85% ethanol for 65 hr. at 30~45°C. We have carried out the reaction in 85% ethanol containing 15% $H_2{}^{18}O$ (enriched by 0.67% ^{18}O) and found that the resulting *o*-hydroxyazobenzene incorporated very little excess ^{18}O from the medium (CO_2 found, 0.213% of ^{18}O, tank CO_2, 0.204% ^{18}O). We favor that the reaction proceeds through an intramolecular oxygen radical shift from *N*-oxide. A similar free radical shift is known in the reaction of dimethylaniline-*N*-oxide with acetic anhydride[10].

Further work is in progress in this laboratory to elucidate the mechanism using ^{18}O-labeled azoxybenzene. Details of this work and further work will be published shortly.

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[4] M. M. Shemyakin, V. J. Maimind and Ts. E. Agadzhanyan, *Chem. & Ind.*, **1961**, 1223.

[5] P. H. Gore, ibid., **1959**, 191.

[6] a) "Name Reactions in Organic Chemistry" (Jinmei Yuki-Hanno-Shu), Vol. II, Ed. by M. Murakami and Y. Yukawa, Asakura Book Co. (1954), p. 228.
b) C. K. Ingold, "Structure and Mechanism in Organic Chemistry", Cornell Univ. Press (1953), p. 621.

[7] Y. Yukawa, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **71**, 603 (1950).

[8] S. Okazaki and M. Okumura, unpublished work,— private communication.

[9] a) W. M. Cumming and G. S. Ferrier, *J. Chem. Soc.*, **127**, 2374 (1925).
b) G. M. Badger and R. G. Buttery, ibid., **1954**, 2243.

[10] S. Oae, T. Kitao and Y. Kitaoka, 12th. Mechanism Conference Reports, the Chemical Society of Japan, Sendai, October, 1961.