

Potentials eine wesentliche Verkleinerung des Dunkelstromes erreicht werden kann (Nr. 5).

Der typische Verlauf des Dunkelstromes in Abhängigkeit des angelegten Potentials ist in Abbildung 1 wiedergegeben.

Es ist interessant noch zu bemerken, dass bei einigen (nicht bei allen) untersuchten Photomultipliern ein Hysteresis-Effekt, wie er in Abbildung 2 dargestellt ist, beobachtet wurde.

Der Wert des Dunkelstromes für eine bestimmte Spannung war in einem bestimmten Bereich verschieden, je nachdem in einer steigenden oder fallenden Spannungsreihenfolge gemessen wurde, trotzdem die Zeitintervalle zweier aufeinanderfolgender Messpunkte 10 min waren. Dieser Effekt hängt wahrscheinlich mit einer von gestreuten Elektronen erzeugten Lumineszenz des Glaskolbens zusammen.

J. LINDER und E. LÜSCHER

Optisches Labor Metrohm S.A., Herisau-Lausanne, den 15. Oktober 1956.

Summary

The influence of an exterior electrical field on the dark current of RCA-photomultipliers has been studied and a hysteresis effect has been observed. The exterior field causes a diminution of the dark current only on tubes with very high "normal" dark current.

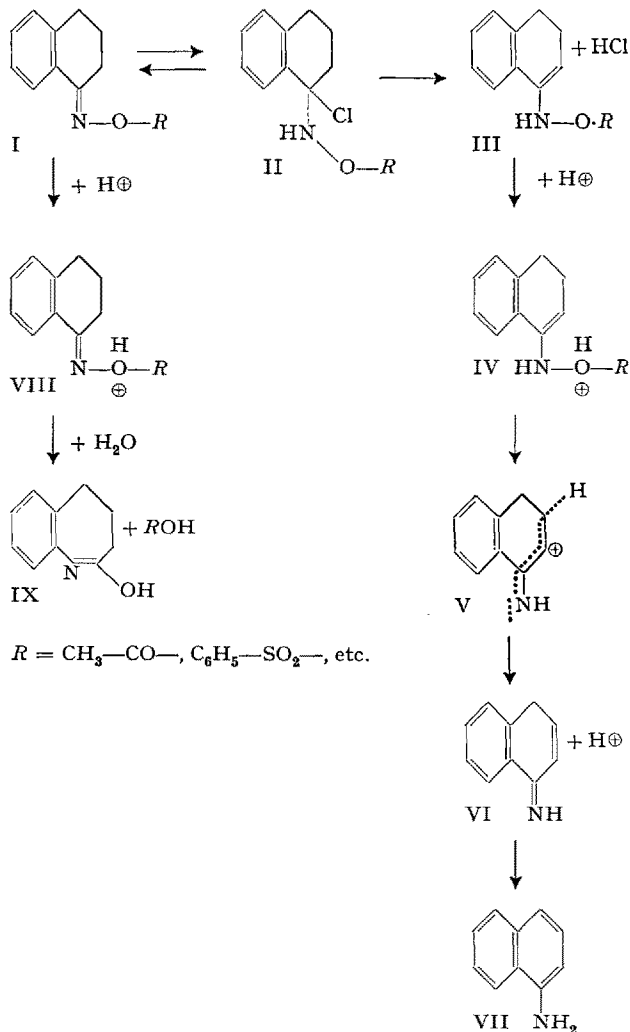
Abnormal Beckmann Rearrangements A Mechanism of the Semmler Reaction

The "Wolff" aromatization reaction¹ owes its origin to SEMMLER². In view of a recent publication³ on this subject our views on the mechanism are presented, as work on this reaction is in progress.

In our opinion, the reaction takes place as a result of the abnormal decomposition of the oxime ester salt (II) itself⁴. It is postulated that this salt decomposes in two distinct ways, viz:

(1) the normal Beckmann rearrangement, which is generally a fast change, the overall velocity of which depends upon the electron attracting capacity of the group R^5 .

(2) the Semmler rearrangement, which is kinetically slower but thermodynamically favoured because of the endocyclic double bond in III as against the exocyclic bond in I⁶ and the release of resonance energy by the formation of VII. It is suggested that protonation of the hydroxylamine derivative III, results in the formation of a mesomeric cation V which stabilizes itself by the release of a proton resulting in VII, through VI.



According to the present mechanism use of drastic conditions⁷ or having a strongly electron attracting group like $\text{C}_6\text{H}_5\text{-SO}_2\text{-}$ ⁸ should favour the former course, at the expense of the latter. This is in conformity with experiment. A similar mechanism is envisaged for the aromatization of monocyclic α, β -unsaturated ketone oximes⁹.

M. V. BHATT

Department of Organic Chemistry, Indian Institute of Science, Bangalore, India, October 4, 1956.

Résumé

Un mécanisme pour la réaction de SEMMLER («Wolff Aromatisation») a été proposé.

¹ L. WOLFF, M. GABLER, and F. HEYL, *Ann.* **322**, 362, 380 (1902).

² W. SEMMLER, *Ber. dtsh. chem. Ges.* **25**, 3352 (1892).

³ A. HARDY, E. R. WARD, and L. A. DAY, *J. chem. Soc.* **1956**, 1979.

⁴ When the acyl radical is strongly electron attracting e.g. $R = \text{C}_6\text{H}_5\text{-SO}_2\text{-}$ no salt of the type II may be formed as the oxime ester undergoes normal Beckmann change.

⁵ B. JONES, *Chem. Rev.* **35**, 335, 337 (1944).

⁶ H. C. BROWN, J. H. BREWSTER, and H. SHECHTER, *J. Amer. chem. Soc.* **76**, 467 (1954).

⁷ E. C. HORNING, V. L. STROMBERG, and H. A. LLOYD, *J. Amer. chem. Soc.* **74**, 5153 (1952).

⁸ G. SCHROETER, *Ber. dtsh. chem. Ges.* **63**, 308 (1903).

⁹ L. WOLFF, M. GABLER, and F. HEYL, *Ann.* **322**, 362, 380 (1902). - E. C. HORNING, V. L. STROMBERG, and H. A. LLOYD, *J. Amer. chem. Soc.* **74**, 5153 (1952).