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CCCIII.—The Supposed Formation of 1:2:4-Oxadiimine Rings from Nitroso-compounds and Methylenearylamines.

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INGOLD prepared a number of compounds by the action of nitrosobenzenes on methyleneanilines (J., 1924, 125, 93 et seq.). He ascribed to the products a ring structure, $ArN < CH_2 > NAr'$, and asserted that the facts were totally contrary to "the hypothesis by means of which so many obscure facts in chemistry are nowadays ' explained '" (loc. cit., p. 93).

He subsequently discovered that his products were not ring compounds at all, but N-hydroxyamidines. In a paper with Farrow (J., 1924, **125**, 2543), he maintained, nevertheless, that cycloids are formed in the first instance and that these cycloids isomerise to hydroxyamidines at the moment of their formation (*loc. cit.*, p. 2545):



The proof given was that "the substances obtained in the two ways shown by the equation above are, in each case, identical with one of the pair of isomerides prepared by Comstock and Clapp's reaction."

Only one such case, however, was described, namely, that where $Ar = C_6H_4Br(p)$ and $Ar' = C_6H_4Cl(p)$ (Ingold, *loc. cit.*, p. 101), an unsatisfactory pair in view of the close chemical relationship and likely isomorphism of their derivatives.

Farrow and Ingold also referred to the case where $Ar = C_6H_5$ and $Ar' = C_6H_4 \cdot CH_3(p)$; but here the product was made in only one of the ways indicated in the above scheme, namely, from $CH_2:N \cdot C_6H_4 \cdot CH_3(p)$ and $O:N \cdot C_6H_5$. It is most significant that the product was identified with $N(C_6H_4 \cdot CH_3):CH \cdot N(C_6H_5) \cdot OH$, which on alkaline hydrolysis gave *azoxybenzene* with no trace of azoxytoluene (*loc. cit.*, p. 2551-2552) and p-toluidine. Here, be it noted, the aromatic radical in the original *nitroso*-compound reappears in attachment to *oxidised nitrogen* and the other, originally as methylene*amine*, as pure amine with *unoxidised nitrogen*.

Returning to the crucial case where $Ar = C_8H_4Br$ and

 $Ar' = C_6H_4Cl$: a product A, made from chloronitrosobenzene and methylenebromoaniline, was identified with another, B, made from bromonitrosobenzene and methylene-*p*-chloroaniline (Ingold, *loc. cit.*), and both with a third product, C, which was made in quite a different way and certainly had the structure

 $C_6H_4Cl\cdot N(OH)\cdot CH:N\cdot C_6H_4Br.$

The last-mentioned gave pure *p*-bromoaniline when hydrolysed by alkali (Farrow and Ingold, *loc. cit.*, 2551, 2552).

The present authors had good theoretical reasons for thinking it unlikely that such a ring would be formed at all in the addition process, and still more unlikely that such a ring, once formed, would break down exclusively in one direction. They therefore took up the re-examination of the product obtained by Ingold's method from p-chloromethyleneaniline and p-bromonitrosobenzene. Observing that, even after recrystallisation from benzene, the product was not very well defined, and remembering that it might be isomorphous with its isomeride (from which it differs only in the interchange of place of chlorine and bromine), they decided to hydrolyse it with aqueous-alcoholic sodium hydroxide in the general way described by Farrow and Ingold (loc. cit., pp. 2547, 2548) and to examine the substituted aniline so formed. The resulting base solidified at once; even before recrystallisation it melted 67-69°, and after one crystallisation from light petroleum at 68.5-69°. (A sample of pure p-chloroaniline obtained from British Drug Houses Limited melted after similar treatment at 69.5--70°; and a sample of pure p-bromoaniline after similar treatment at $62 - 62 \cdot 5^{\circ}$.)

We are indebted to Dr. E. Chapman, who has had much experience in the determination of halogen by Robertson's method, for an analysis of the base. 0.1068 Gram of the compound gave halogen equivalent to 8.23 c.c. of N/10-AgNO₃. Formula C₆H₆NCl requires 8.37 c.c. and C₆H₆NBr requires 6.21 c.c.

It is thus clear that the base was mainly *p*-chloroaniline; the authors thought they detected a very small quantity of bromine in a careful qualitative test, but this would not be very surprising, as some reduction of the bromoazo-compounds during the original hydrolysis seemed quite possible.

It is evident that a compound which yields mainly p-chloroaniline cannot possibly be identical with one which, as Farrow and Ingold stated, yields p-bromoaniline with no trace of p-chloroaniline. That such a mistake could ever have been made is proof that the evidence on which Ingold relied was not trustworthy and it cannot be admitted that there is any good reason to suppose that his cycloids are formed at any stage.

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If Farrow and Ingold are disposed to maintain their original view, then the onus of proof rests with them. An obvious and acceptable line of proof would be for them to prepare their compounds by both the methods in the scheme on p. 2234 and to show that these then give the same products in the same proportion when hydrolysed.

In conclusion, the facts, so far as they have yet been fully established, are entirely consistent with polarity theories, all previous statements to the contrary notwithstanding (*inter alia*, Ingold, J., 1924, 125, 93; Ingold and Weaver, *ibid.*, pp. 1457-1459).

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