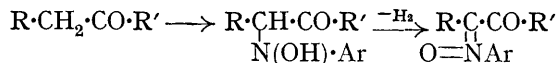


## NOTE.

*Reactive Methylene Groups and Nitroso-compounds.* By ERNST BERGMANN.

SCHOENBERG and MICHAELIS (this vol., p. 627) report the formation of a nitron from 3:3-diphenylhydrindone and nitrosobenzene or *p*-nitrosodimethylaniline, and suggest the following most reasonable mechanism:



The analogous reaction was observed by Leiser and the author some years ago in the case of fluorene and 2:7-dibromofluorene, which react with *p*-nitrosodimethylaniline to give *p*-dimethylaminophenyldiphenylenemethylenenitron and its 2':7'-dibromo-derivative, respectively, instead of the anil, as supposed by Novelli (*Centr.*, 1928, I, 1410). Fluorene (3 g.) and *p*-nitrosodimethylaniline (3 g.) in alcohol (300 c.c.) were boiled with sodium ethoxide (sodium, 0.46 g.; alcohol, 40 c.c.) for 4 hours; the mass was diluted with water, extracted with ether, and the resinous ethereal residue triturated with acetone at 0°. The crystalline product, recrystallised from propyl alcohol, formed quadrilateral prisms, m. p. 224° (decomp.), identical with the nitron, prepared from 9-chlorofluorene and nitrosodimethylaniline (Bergmann and Hervey, *Ber.*, 1929, 62, 893) (Found: N, 8.8. Calc. for C<sub>21</sub>H<sub>18</sub>ON<sub>2</sub>: N, 8.9%).

In the same way, 2:7-dibromofluorene (Siegltitz, *Ber.*, 1920, 53, 1236) gave *p*-dimethylaminophenyl-2':7'-dibromodiphenylenemethylenenitron, which crystallised spontaneously from the reaction mixture and was collected and washed with methanol; brown-violet needles, from anisole, m. p. 224° (decomp.) (Found: C, 53.8; H, 3.5; N, 5.9; Br, 33.6. C<sub>21</sub>H<sub>16</sub>ON<sub>2</sub>Br<sub>2</sub> requires C, 53.4; H, 3.4; N, 5.9; Br, 33.9%). In both cases, the mother-liquors contain azoxydimethylaniline, which is the main product—apparently formed by direct interaction between the nitroso-compound and the ethoxide (Ehrlich and Sachs, *Ber.*, 1899, 32, 2341; Hantzsch and Lehmann, *Ber.*, 1902, 35, 905)—when the reaction is carried out in benzene solution.

The mechanism suggested by Schoenberg and Michaelis accounts for the formation of deeply coloured products from 9-methylacridine and *p*-nitrosodialkylanilines (Kaufmann and Vallette, *Ber.*, 1912, 45, 1736; Porai-Koschitz, Auschkap, and Amsler, *Centr.*, 1911, II, 289); these products probably contain two hydrogen atoms less than assumed by the previous authors and should be formulated as in (I). In these cases the formation of the expected anils among the products was also reported. We were unable to isolate the *anil* from the reaction between fluorene and *p*-nitrosodimethylaniline, but we prepared it by boiling fluorenone (2.7 g.) and *p*-dimethylaminoaniline (4.2 g.) with a few drops of dilute hydrochloric acid (Reddelien, *Ber.*, 1913, 46, 2718). The red resin so obtained was triturated with methanol, and crystallised from alcohol, forming red prisms, m. p. 100° (Found: C, 84.4; H, 6.2. C<sub>21</sub>H<sub>18</sub>N<sub>2</sub> requires C, 84.5; H, 6.0%).

Finally, it is suggested that nitron formation from safole and nitrosobenzene (Alessandri *et al.*, *Centr.*, 1910, II, 302; 1915, I, 1210) is also based on the presence of an activated methylene group, although the reaction proceeds with migration of the double bond. Here again, part of the nitrosobenzene is reduced by the primary product to give azoxybenzene, for the formation of which no satisfactory explanation has hitherto been proposed. This mechanism accounts for the fact that *isosafole* is resistant to the action of nitrosobenzene; although it contains preformed the unsaturated system as present in the end product of the above reaction, yet the necessary reactive methylene group is missing.—THE DANIEL SIEFF RESEARCH INSTITUTE, REHOVOTH (PALESTINE). [Received, June 24th, 1937.]

