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INTERMOLECULAR HYDRIDE TRANSFER IN THE DECOMPOSITION OF ARYL DIAZONIUM TETRAFLUOROBORATES IN N,N-DIMETHYLANILINE

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When o-carboxybenzenediazonium tetrafluoroborate (I; R = CO_2H) is made to decompose in an excess of hot N,N-dimethylaniline, 4,4'-bisdimethylaminodiphenylmethane m.p. 87° (1) (II; R = Me; 40%), the tetramethylbenzidine m.p. 198° (III; 13%), the diphenylmethane m.p. 56°(2) (II; R = H; 15%) and N-methylaniline (20.6%) are produced. The diphenylmethane (II; R = H) had absorption bands at 3350 (NH) and 808 cm^{-1} (para-substitution) and its n.m.r. spectrum in $CDCl_3$ showed peaks at τ 7.22 (3 protons, NMe) τ 7.13 (6 protons, NMe_2) and τ 6.22 (2 protons, $-CH_2-$). A peak at τ6.79 (1 proton, NH) was removed on deuteration. The aromatic protons appeared as a complex of two overlapping A_2B_2 systems (8 protons) with high-field protons at τ3.45 and 3.31 (J = 9 c./sec.) and low field protons at τ2.98 (J = 9 c./sec.). Boron trifluoride which is liberated during the decomposition is not responsible for the reaction because when made to react with hot dimethylaniline it gives only the known addition complex (3). N,N-Dimethyl-p-toluidine does not give any of the above products which suggests that the para-methyl group vitiates the course of the reaction. Much research has been carried out recently on the reaction of N,N-dimethylaniline and benzoyl peroxide in solvents (4). The dimethylaminodiphenylmethane (II; R = Me) has been found to be one of the products and is thought to arise via an ionic mechanism involving the quaternary salt $[(PhNMe_2.O.COPh)^+ \ PhCO_2^-]$ as intermediate. Other routes have, however, been suggested (cf. 4 a and refs. cited therein).

The uncatalysed decomposition of aryl diazonium fluoroborates in solvents which is the type of reaction under discussion is ionic in character (5) as it generates a phenyl cation, nitrogen and boron trifluoride. Formation of the diphenylmethanes (II; R = Me and R = H) can be envisaged in our case to involve first a hydride abstraction from the N-methyl group by the carbonium ion to give the mesomeric ion (IV) (cf. scheme) which under BF_3 catalysis reacts with dimethylaniline to produce the intermediate (V). The latter compound has in fact been isolated by Swan and co-workers (4a) from the aforementioned reaction of benzoyl peroxide and dimethylaniline. Its conversion into the diphenylmethane (II; R = Me) by heating in dimethylaniline was also demonstrated (4a). Under our conditions isolation of the intermediate (V) was not possible because firstly of the high temperature required for pyrolysing the diazo-salt and secondly of the presence of BF_4^- which favours the rearrangement of the intermediate Mannich type base (V) into the diphenylmethane (II) (cf. Scheme c). The previously mentioned isolation of N-methylaniline supports this mechanism and also accounts for the formation of the other diphenylmethane (II; R = H).

Additional evidence for hydride ion abstraction was provided by the fact that we obtained almost exclusively benzoic acid from the decomposition of the tetrafluoroborate (I; R = CO_2H) in dimethylaniline instead of o-fluorobenzoic acid, the product normally expected from a Schiemann reaction (5). The presence of the benzidine (III) is presumably due to a concomitant but much less extensive homolysis of the tetrafluoroborate (5) to give aryl radicals (Ar.). These in turn produce some p-NMe_2.Ph. radicals by H-abstraction, which by a radical pairing process form the benzidine (III). Decomposition of benzenediazonium tetrafluoroborate (I; R = H) in dimethyl aniline gave the same products (II; R = Me, 6.3%) (III; 0.5%) as the pyrolysis of the carboxylic acid (I; R = CO_2H). The marked reduction in the yields appears to be due to substantial formation of the azo-compound Ph.N:N-C_6H_4.NMe_2-p. This discrepancy in the behaviour of the two diazo-compounds may be explained by initial salt formation between dimethylaniline and the carboxylic acid (I; R = CO_2H) which deactivates the base towards the process of electrophilic azocoupling. Alternatively intramolecular hydrogen bonding in the carboxylic acid (I; R = CO_2H) would impair the reactivity of the diazo-group.

Attempts to extend the reaction to N,N-diethylaniline gave tarry products and predominantly benzoic acid which again demonstrates hydride transfer. In this case the carbonium ion produced $[Ph.N(Et).\overset{+}{C}H\text{-}CH_3]$ could feasibly lose a proton to form the enamine $[Ph.N(Et).CH{=}CH_2]$ with subsequent polymerisation favoured by the reaction conditions (BF_3).

All compounds were identified by elemental analysis by a study of their appropriate spectra and in some cases by comparison with unambiguously prepared samples.

By contrast, intramolecular hydride shifts involving diazonium compounds are often geometrically favoured and, therefore, well documented. For instance recently Cohen and co-workers (6) have described an internal H-transfer from an N-Me group to a diazonium intermediate in an N,N-disubstituted benzamide as set out (VI ⟶ VIII). The intermediate (VII) analogous to the carbonium ion (IV) in our reaction, suffered hydrolysi because of the aqueous medium before it could undergo further changes.

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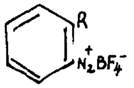


I

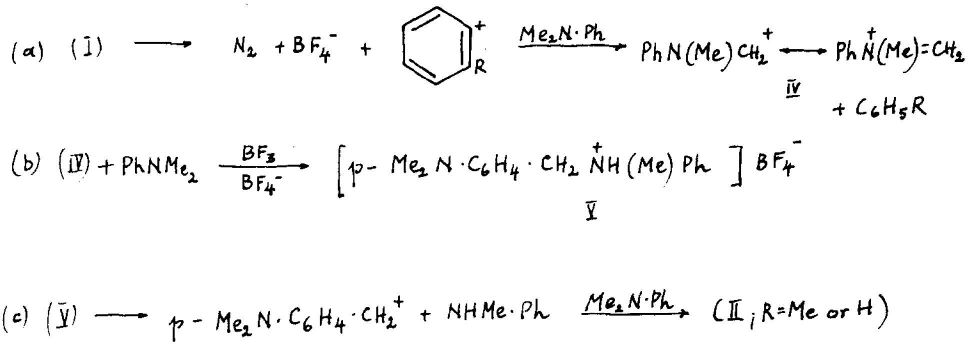
$p\text{-}Me_2N\cdot C_6H_4\cdot CH_2\cdot C_6H_4\cdot NMeR\text{-}p$

II

$p\text{-}Me_2N\cdot C_6H_4\cdot C_6H_4\cdot NMe_2\text{-}p$

III

Scheme :



$$(a)\ (I) \longrightarrow N_2 + BF_4^- + \ldots$$

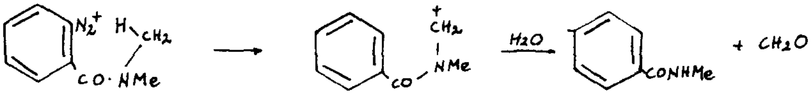
$$(a)\ \ldots \xrightarrow{Me_2N\cdot Ph} PhN(Me)\overset{+}{C}H_2 \longrightarrow Ph\overset{+}{N}(Me){=}CH_2 + C_6H_5R$$

IV

$$(b)\ (IV) + PhNMe_2 \xrightarrow[BF_4^-]{BF_3} [p\text{-}Me_2N\cdot C_6H_4\cdot CH_2\overset{+}{N}H(Me)Ph]\,BF_4^-$$

V

$$(c)\ (V) \longrightarrow p\text{-}Me_2N\cdot C_6H_4\cdot \overset{+}{C}H_2 + NHMe\cdot Ph \xrightarrow{Me_2N\cdot Ph} (II;\ R{=}Me\ \text{or}\ H)$$



VI VII VIII

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