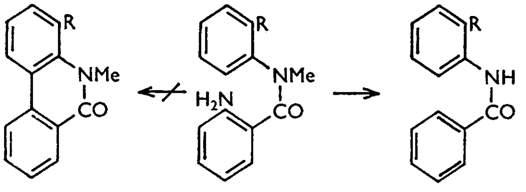
824. *Internuclear Cyclisation. Part XV.** *The Catalytic Decomposition of Diazonium Chlorides prepared from* ortho-*Substituted 2-Amino-*N-*methylbenzanilides.*

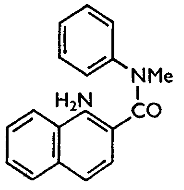
By D. H. Hey and R. A. J. Long.

Catalytic decomposition of the diazonium chlorides prepared from three 2-amino-*N*-methylbenzanilides, which have a substituent (Me, NO_2, or OMe) at the *ortho*-position with respect to the amino-group, provide examples of demethylation and deamination without phenanthridone formation, phenanthridone formation without demethylation and deamination, and concomitant demethylation and deamination with phenanthridone formation. The factors influencing the courses of these reactions are being further investigated.

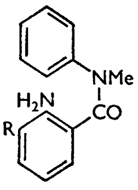
Earlier [1] it was reported that the decomposition of diazonium salts prepared from *ortho'*-substituted 2-amino-*N*-methylbenzanilides (I) did not give ring-closed products (II), but only products arising from the replacement of both the diazonium group and the *N*-methyl group by hydrogen (III). A further example of this abnormal reaction leading to simultaneous deamination and demethylation was later reported in the decomposition of the diazonium chloride prepared from *N*-(1-amino-2-naphthoyl)-*N*-methylaniline (IV), which gave 2-naphthanilide.[2] The formation of this compound from a starting compound which did not contain a substituent atom or group at the *ortho*-position to the :NMe group was unexpected. The reason for the anomalous reactions with *ortho'*-substituted *N*-methylbenzanilides was considered to be steric in character, interference between the substituent R and the *N*-methyl group causing enforced proximity of the *N*-methyl group to the diazonium group. This was considered to result in the replacement of the latter by a hydrogen atom supplied by the methyl group; it is noteworthy that the decomposition of the diazonium salt prepared from *N*-2'-amino-4',5'-methylenedioxybenzoylindoline led to the formation of a compound regarded as 4',5'-methylenedioxybenzoylindole.[3] The formation of this compound supports the view that the replacement of the diazonium group by hydrogen takes place at the expense of a methyl or methylene group attached to the nitrogen atom.



(II) (I) (III)



(IV)



(V)

The unexpected formation of 2-naphthanilide as a product of the decomposition of the diazonium salt prepared from *N*-(1-amino-2-naphthoyl)-*N*-methylaniline (IV) suggested that similar steric factors might be operative with a substituent atom or group at the *ortho*-position to the diazonium group in compounds derived from 2-amino-*N*-methylbenzanilides (V). Reactions have therefore been carried out with the diazonium chlorides prepared from three *N*-methylbenzanilides which carry such substituent groups. The decompositions were carried out in acid media at room temperature with the addition of copper powder.

---

* Part XIV, *J.*, 1959, 2254.

[1] Hey and Turpin, *J.*, 1954, 2471.

[2] Abramovitch, Hey, and Long, *J.*, 1957, 1781.

[3] Cook, Loudon, and McCloskey, *J.*, 1954, 4176.

Condensation of 3-methyl-2-nitrobenzoyl chloride with aniline gave 3-methyl-2-nitrobenzanilide, which was methylated with dimethyl sulphate to give 3,*N*-dimethyl-2-nitrobenzanilide, which was also prepared from 3-methyl-2-nitrobenzoyl chloride and methylaniline. Reduction of the 3,*N*-dimethyl-2-nitrobenzanilide gave the amine (V; R = Me), which was diazotised in the presence of hydrochloric acid and decomposed at room temperature with the addition of copper powder. 3-Methylbenzanilide was isolated together with an acidic by-product. 2-Amino-*N*-methyl-3-nitrobenzanilide (V; R = NO_2) was prepared from 3-nitroanthranilic acid and phosphorous tri-(*N*-methylanilide) by an extension of Grimmel, Guenther, and Morgan's method.[2,4] Decomposition of the diazonium chloride gave *N*-methyl-5-nitrophenanthridone and a by-product, m. p. 240°, but neither 3-nitrobenzanilide nor *N*-methyl-3-nitrobenzanilide. 3-Methoxy-2-nitrobenzanilide was prepared from 3-methoxy-2-nitrobenzoyl chloride and methylaniline. The amine (V; R = OMe) obtained on reduction was diazotised, and decomposition of the diazonium chloride gave *N*-methyl-5-methoxyphenanthridone and 3-methoxybenzanilide.

Amine (V)	Phenanthridone (%)	Demethylation and deamination (%)
R = Me	0	20
R = NO_2	13	0
R = OMe	18	5

The tabulated results obtained with these three amines indicate that factors other than steric hindrance must be involved. It is possible that the experimental conditions under which diazotisation was carried out may account in part for these results; these factors are being further investigated.

EXPERIMENTAL

3-*Methyl*-2-*nitrobenzanilide*.—3-Methyl-2-nitrobenzoic acid (3·7 g.), prepared by Jürgens' method,[5] was boiled under reflux with thionyl chloride (5 ml.) for 2 hr. Excess of thionyl chloride was removed under reduced pressure, and to the cold acid chloride was added pyridine (5 ml.) and then aniline (1·9 g.), After 1 hr. the mixture was heated on a water-bath. It was then poured into water and the solid which separated was crystallised from ethanol to give 3-*methyl*-2-*nitrobenzanilide* (4·0 g.) in needles, m. p. 148—149° (Found: C, 65·1; H, 4·6. $C_{14}H_{12}O_3N_2$ requires C, 65·1; H, 4·7%).

3,N-*Dimethyl*-2-*nitrobenzanilide*.—(i) A solution of the above anilide (4·0 g.) in acetone (40 ml.) was boiled under reflux with sodium hydroxide (8·0 g.) in water (40 ml.), while dimethyl sulphate (8·0 ml.) was added dropwise. Boiling was continued for 20 min., after which the mixture was poured into water. Recrystallisation of the precipitated solid from ethanol gave 3,N-*dimethyl*-2-*nitrobenzanilide* (3·9 g.) in pale yellow needles, m. p. 123° (Found: C, 66·6; H, 5·3. $C_{15}H_{14}O_3N_2$ requires C, 66·7; H, 5·3%). (ii) To the acid chloride prepared as above from 3-methyl-2-nitrobenzoic acid (1·4 g.) was added ice-cold pyridine (5 ml.) and then *N*-methylaniline (0·83 g.). After 1 hr. the mixture was heated on a water-bath for a further hour and then diluted with water. Recrystallisation of the solid which separated gave 3,*N*-dimethyl-2-nitrobenzanilide (1·2 g.) in pale yellow needles, m. p. 123°, from ethanol identical with the product obtained by method (i).

2-*Amino*-3,N-*dimethylbenzanilide Hydrochloride*.—The nitro-compound (3·9 g.) in methanol (50 ml.) was shaken with 5% palladium–charcoal in the presence of hydrogen. When the required volume had been absorbed, the mixture was filtered and the solvent was removed under reduced pressure. The residue dissolved in ether was added to ethereal hydrogen chloride. The *amine hydrochloride* (3·3 g.) which separated crystallised from ethanol–ether in needles, m. p. 199° (Found: C, 64·8; H, 6·0. $C_{15}H_{16}ON_2$,HCl requires C, 64·8; H, 6·1%).

Decomposition of the Diazonium Chloride prepared from 2-*Amino*-3,N-*dimethylbenzanilide*.—A solution of the amine hydrochloride (3·3 g.) in concentrated hydrochloric acid (5 ml.) and water (150 ml.) was diazotised at 0° with a solution of sodium nitrite (1·0 g.) in water (10 ml.). After 1 hr. copper powder (1·0 g.) was added. Stirring was continued for 3 hr., after which the solution no longer gave a positive test with alkaline 2-naphthol. The mixture was filtered and

[4] Grimmel, Guenther, and Morgan, *J. Amer. Chem. Soc.*, 1946, **68**, 539.

[5] Jürgens, *Ber.*, 1907, **40**, 4409.

both filtrate and residue were extracted with chloroform. The combined extracts were washed with aqueous sodium hydroxide and water and then dried (Na_2SO_4). Removal of the chloroform left a pale brown gum, which was dissolved in benzene and adsorbed on an alumina column. Elution with benzene–light petroleum (b. p. 40—60°) (2 : 1; 150 ml.) gave a yellow gum (0·08 g.). Further elution with the same solvent (150 ml.) followed by benzene (250 ml.) gave a solid which on recrystallisation from aqueous ethanol afforded 3-methylbenzanilide (0·6 g.) in needles, m. p. and mixed m. p. 125° (Bachmann and Barton [6] give m. p. 125—125·5°) (Found: C, 79·6; H, 6·1. Calc. for $C_{14}H_{13}ON$: C, 79·8; H, 6·2%). Further elution of the column with benzene, and with ether–ethanol, afforded a series of pale brown gums (0·9 g.). Acidification of the alkaline washings gave a solid (0·4 g.) which crystallised from ethanol in needles, m. p. 239° (Found: C, 70·5; H, 5·7%).

2-*Amino*-N-*methyl*-3-*nitrobenzanilide*.—3-Nitroanthranilic acid (1·3 g.), prepared by Chapman and Stephen's method,[7] in a suspension of phosphorous tri-(*N*-methylanilide) [2] (1·3 g.) in dry toluene (50 ml.) was boiled under reflux for 2 hr. The hot solution was decanted from the metaphosphorous acid and washed successively with 2N-aqueous sodium hydroxide and 2N-hydrochloric acid. Removal of the toluene under reduced pressure left a yellow oil which solidified. Crystallisation from ethanol gave 2-*amino*-N-*methyl*-3-*nitrobenzanilide* (1·4 g.) in orange prisms, m. p. 109° (Found: C, 62·2; H, 5·1. $C_{14}H_{13}O_3N_3$ requires C, 62·1; H, 4·8%).

Decomposition of the Diazonium Chloride prepared from 2-*Amino*-N-*methyl*-3-*nitrobenzanilide*.—The amine (2·0 g.), in ethanol (60 ml.) and concentrated hydrochloric acid (20 ml.), was diazotised with pentyl nitrite (3 ml.) at 0°. After 1 hr. the solution was diluted with cold water (120 ml.) and filtered. More water (100 ml.) and urea (2 g.) were added to the filtrate. After 10 min. copper powder (2 g.) was added. Nitrogen was evolved and a white solid began to separate. After 30 minutes' stirring the reaction was complete and the mixture was filtered. Both filtrate and residue were extracted with chloroform. The extracts were combined, washed with aqueous sodium hydroxide and with water, and dried (Na_2SO_4). Removal of the chloroform left a gum (1·8 g.), which was dissolved in a small volume of benzene and adsorbed on an alumina column. Elution with benzene–light petroleum (b. p. 40—60°) (3 : 1; 800 ml.) gave a pale yellow solid, which on recrystallisation from ethanol afforded N-*methyl*-5-*nitrophenanthridone* (0·25 g.) in pale yellow needles, m. p. 189° ($\lambda_{max.}$ 227, 261, 320, 333 mμ. 10^{-3} ε 49·56, 13·32, 5·27, 6·503) (Found: C, 66·2; H, 4·1. $C_{14}H_{10}O_3N_2$ requires C, 66·2; H, 4·0%). Further elution with benzene (200 ml.) and benzene–ether (1 : 1) (600 ml.) gave a yellow gum (0·1 g.), while with ether (600 ml.) and chloroform (400 ml.) a red gum was obtained from which an amorphous solid (0·3 g.), m. p. 240°, was isolated on trituration with ethanol (Found: C, 63·8; H, 4·6%). Further elution with ethanol gave a red gum (0·3 g.). Acidification of the alkaline washings gave only a trace of tar.

N-*Methyl*-3-*nitrobenzanilide*.—Pyridine (10 ml.) and methylaniline (1·3 g.) were added to 3-nitrobenzoyl chloride, prepared from the acid (2 g.) at 0°. The mixture was heated on a boiling-water bath for 1 hr. and then poured into water. Recrystallisation from ethanol of the resulting solid gave N-*methyl*-3-*nitrobenzanilide* (2·1 g.) in cubic crystals, m. p. 109° (Found: C, 66·5; H, 4·8. $C_{14}H_{12}O_3N_2$ requires C, 66·2; H, 4·7%). A similar procedure with aniline (1·2 g.) gave 3-nitrobenzanilide (2·2 g.) in needles, m. p. 153°.

3-*Methoxy*-N-*methyl*-2-*nitrobenzanilide*.—3-Methoxy-2-nitrobenzoic acid (4·0 g.) prepared by Albert and Hampton's method,[8] was boiled under reflux for 1 hr. with thionyl chloride (10 ml.). The excess of thionyl chloride was removed under reduced pressure. Pyridine (10 ml.) was added at 0° to the crude acid chloride, followed by *N*-methylaniline (2·2 g.). The solution was heated on a boiling-water bath for 1 hr. and then poured into ice–water (200 ml.). Recrystallisation of the solid which separated gave 3-*methoxy*-N-*methyl*-2-*nitrobenzanilide* (4·4 g.) in pale yellow needles, m. p. 160—161°, from ethanol (Found: C, 62·8; H, 4·9. $C_{15}H_{14}O_4N_2$ requires C, 63·0; H, 5·0%).

2-*Amino*-3-*methoxy*-N-*methylbenzanilide*.—The nitro-compound (3·5 g.), in warm ethanol (200 ml.) containing 5% palladium–charcoal (0·5 g.), was shaken with hydrogen at atmospheric pressure. After the absorption of the required volume the mixture was filtered and the filtrate was evaporated under reduced pressure. Recrystallisation of the solid residue from ethanol

---

[6] Bachmann and Barton, *J. Org. Chem.*, 1938, **3**, 300.
[7] Chapman and Stephen, *J.*, 1925, 1795.
[8] Albert and Hampton, *J.*, 1952, 4988.

gave 2-*amino*-3-*methoxy*-N-*methylbenzanilide* (2·3 g.) in cubic crystals, m. p. 92—93° (Found: C, 70·5; H, 6·0. $C_{15}H_{16}O_2N_2$ requires C, 70·5; H, 6·3%).

Decomposition of the Diazonium Chloride prepared from 2-*Amino*-3-*methoxy*-N-*methylbenzanilide*.—The amine (2·2 g.), in concentrated hydrochloric acid (20 ml.) and water (100 ml.), was diazotised with sodium nitrite (1·5 g.) in water (10 ml.) at 0°. Stirring was continued for 2 hr., after which urea (2·0 g.) was added. Copper powder (1·0 g.) was added and the mixture was stirred at room temperature for 3 hr., after which a positive reaction was no longer given with alkaline 2-naphthol. The mixture was filtered and both filtrate and residue were extracted with chloroform. The combined extracts were washed with aqueous sodium hydroxide and with water and then dried (Na_2SO_4). Removal of the chloroform left a pink gum which was dissolved in benzene and adsorbed on an alumina column. Elution with benzene–light petroleum (b. p. 40—60°) (3 : 1; 900 ml.) gave only a trace of gum. Elution with benzene (400 ml.) gave a solid which, on recrystallisation from ethanol, afforded N-*methyl*-5-*methoxyphenanthridone* (0·37 g.) in needles, m. p. 163° ($\lambda_{max.}$ 238, 252, 322, 335 mμ. $10^{-3}\,\varepsilon$ 50·48, 19·38, 6·64, 11·69) (Found: C, 75·3; H, 5·4. $C_{15}H_{13}O_2N$ requires C, 75·2; H, 5·5%). Further elution with benzene–ether (1 : 1) (250 ml.) gave a solid (0·1 g.) which, on recrystallisation from benzene–light petroleum (b. p. 40—60°), gave 3-methoxybenzanilide (0·09 g.) in needles, m. p. and mixed m. p. 118° [see below]. Subsequent elution with ether (400 ml.) gave a yellow gum (0·1 g.) and with ether–chloroform (1 : 1) (400 ml.) a red gum, which on trituration with ethanol afforded a buff amorphous powder (0·1 g.), m. p. 278—279° (Found: C, 75·0; H, 6·1%).

3-*Methoxybenzanilide*.—Pyridine (8 ml.) and then aniline (1·5 g.) were added at 0° to 3-methoxybenzoyl chloride prepared from the acid (2·5 g.). The solution was heated on a boiling-water bath for 1 hr. and then poured into ice–water (100 ml.). The solid which separated crystallised from dilute ethanol to give 3-*methoxybenzanilide* (2·2 g.) in needles, m. p. 118° (Found: C, 74·1; H, 5·7. $C_{14}H_{13}O_2N$ requires C, 74·3; H, 5·9%).

3-*Methoxy*-N-*methylbenzanilide*.—In similar manner the 3-methoxybenzoyl chloride, prepared from the acid (2·5 g.), and methylaniline (1·8 g.) gave 3-*methoxy*-N-*methylbenzanilide* (2·1 g.), which separated from aqueous ethanol in prisms, m. p. 63° (Found: C, 74·7; H, 6·2. $C_{15}H_{15}O_2N$ requires C, 74·5; H, 6·4%).

We thank British Celanese Ltd. for a Studentship (to R. A. J. L.).

KING'S COLLEGE (UNIVERSITY OF LONDON),
STRAND, LONDON, W.C.2.

[*Received, May 25th,* 1959.]