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1,5-Hydrogen Transfer during Diazonium Ion Decomposition[1,2]

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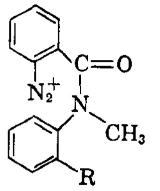
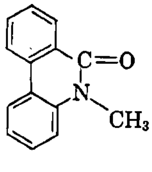
Thermal decomposition of diazonium salt XIIa derived from *o*-amino-*N*,*N*-dimethylbenzamide produced *N*-methylbenzamide (XIIIa) and formaldehyde in equivalent amounts, in addition to a lower yield of *N*-methylphthalimidine (XV). Under similar conditions, the diazonium salt XIIb derived from *o*-amino-*N*,*N*-dibenzylbenzamide gave higher yields of *N*-benzylbenzamide (XIIIb) and benzaldehyde. These results are explained in terms of a 1,5-hydride transfer from the *N*-alkyl group to the positive carbon formed by diazonium ion decomposition. The newly formed cation can then undergo either hydrolysis to an aldehyde and a dealkylated amide or it can suffer internal electrophilic substitution to yield a phthalimidine.

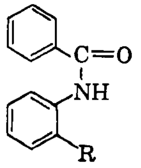
N-Alkylphenanthridones can be conveniently prepared by Pschorr type ring closures of appropriate diazonium salts.[3–7] For example, *N*-methylphenanthridone (II) is prepared by thermal or copper catalyzed decomposition of the diazonium salt Ia derived from *o*-amino-*N*-methylbenzanilide.[3,5] In addition, a number of substituted *N*-methylphenanthridones have been prepared from diazonium ions like I having various substituents *meta* and *para* to the nitrogen in the anilide ring.[4,6] However, when *ortho* substituents are present in this ring, closure to a phenanthridone fails to occur. In these cases, the reaction takes a different course; the diazonium function is replaced by hydrogen and the *N*-methyl group is lost. Thus Ib–g all decompose to the substituted benzanilides IIIb–g.[8,9] The same pattern is followed in the case of the diazonium ion IV, derived from 2-amino-*N*-methylbenz-1′-naphthalide. Upon decomposition, this ion undergoes demethylation rather than ring closure.[8] A case of *N*-deethylation has also been reported.[9]



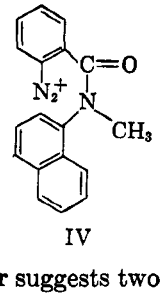
Ia. R = H
b. R = CH_3
c. R = OCH_3
d. R = Cl
e. R = NO_2
f. R = CO_2CH_3
g. R = CO_2H



II



III



IV

This interesting behavior suggests two questions: (i) What is the role of the *ortho* substituent in preventing ring closure? (ii) What is the mechanism of the *N*-dealkylation reaction?

In order to answer the first of these questions it is necessary to consider the detailed course of the ring closure reaction. There is considerable evidence that thermal decompositions of diazonium ions in acid solution occur heterolytically to

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[1] Taken, in part, from the Master's thesis of Raymond M. Moran, Jr., at the University of Pittsburgh, 1959.

[2] This work was supported, in part, by a grant from the National Science Foundation.

[3] A. Pictet and A. Gonset, *Arch. sci. phys. et nat.*, [4], 3, 37 (1897).

[4] H. S. Forrest, R. D. Haworth, A. R. Pinder, and T. S. Stephens, *J. Chem. Soc.*, 1311 (1949).

[5] R. A. Heacock and D. H. Hey, *J. Chem. Soc.*, 1508 (1952).

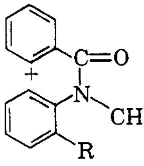
[6] R. A. Heacock and D. H. Hey, *J. Chem. Soc.*, 4059 (1952); 3 (1953).

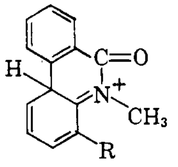
[7] T. R. Govindachari and N. J. Arumugam, *J. Sci. Ind. Res.*, 13B, 694 (1954).

[8] D. H. Hey and D. G. Turpin, *J. Chem. Soc.*, 2471 (1954).

[9] T. R. Govindachari and N. J. Arumugam, *J. Sci. Ind. Res.*, 14B, 250 (1955).

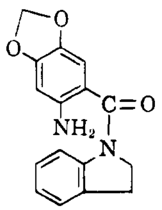
produce carbonium ions.[10] Therefore, it is likely that such decomposition of the diazonium ion Ia yields the carbonium ion Va by loss of nitrogen. This is probably followed by an internal electrophilic substitution into the activated anilide ring to produce the intermediate VIa (one resonance structure is shown). Loss of a proton from VIa reestablishes the aromatic system and yields II.

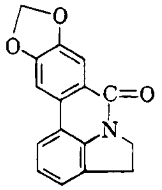

Va. R = H
b. R = CH_3

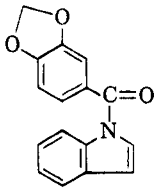

VIa. R = H
b. R = CH_3

However, when a group larger than hydrogen is in the *ortho* position of the anilide ring, the intermediate VI is expected to be destabilized by serious nonbonded repulsion between this substituent and the *N*-methyl group. For example, the two methyl groups of VIb are held almost in the same plane and therefore resemble spatially the methyl groups of 1,8-dimethylnaphthalene. The strain in the latter compound, due to nonbonded repulsion, has been estimated to be 7.6 kcal. per mole.[11]

Strong evidence for this hypothesis would be provided by a demonstration that a diazonium ion in which the two methyl groups of Ib were tied together by a covalent bond could be successfully ring closed. This would lead to an intermediate possessing, as VIb does, a substituent in the *ortho* position of the anilide ring but lacking much of the nonbonded repulsion of VIb. Fortunately, the literature already carries an account of a reaction of this type. In connection with work on the structural proof of alkaloids, Humber *et al.*[12] have thermally decomposed the diazonium salt derived from *N*-(2-amino-4,5-methylenedioxybenzoyl)-2,3-dihydroindole (VII) and have obtained the ring closed product (VIII). This constitutes the first authentic case of a ring closure of a diazonium ion prepared from an *o*-aminobenzanilide possessing an *ortho* substituent in the anilide ring.[13] The fact that the ring-closed product is accompanied by a large amount of the abnormal product *N*-(3,4-methylenedioxybenzoyl)pyrrole (IX) probably indicates that some strain is still present in the transition state for ring closure (*vide infra*).

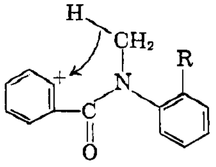

VII

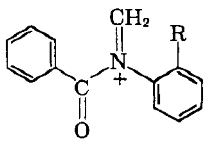

VIII


IX

In order to answer the second question concerning the nature of the dealkylation reaction, we must consider the fact that dealkylation is accompanied by replacement of the nitrogen of the diazonium group by hydrogen. It seems reasonable to assume *a priori* that the hydrogen is supplied by the *N*-alkyl group, as this would provide a starting point for the process by which the carbon-nitrogen bond is destroyed. The fact that no product has ever been reported in which the nitrogen has been replaced by hydrogen and yet in which the *N*-alkyl group is still intact (for example, Ib yields no *N*-methylbenztoluide) indicates further that the reduction of the diazonium function is an intramolecular process. The formation of IX during decomposition of the diazonium ion derived from VII also provides evidence for this viewpoint.

The most favorable mode of reduction in this case would probably involve the transfer of a hydride ion from the *N*-methyl group to the positive carbon of the benzene ring as in *X*. Many examples are known of hydride transfers to carbonium ions,[14] and evidence has recently been presented that intermolecular hydride ion transfer processes are involved in the reduction of diazonium ions by alcohols,[15a] ethers,[15b] and tertiary amines[15b] under certain conditions. In the present case, the hydride transfer is favored by the proximity of the hydrogen to the carbonium ion and by the relative stability of the positive ion (XI) which is generated. The latter ion would be expected to hydrolyze to formaldehyde and a substituted benzanilide. The identity of the carbon fraction lost in this reaction has, however, never been investigated.


X


XI

Because our hypothesis assigns no role to the *N*-phenyl group which was present in all of the compounds which have been previously found to

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(10) For a summary of the evidence and recent references, see D. F. DeTar, *Org. Reactions*, 9, 405 (1957).

(11) J. Packer, J. Vaughn, and E. Wong, *J. Am. Chem. Soc.*, 80, 905 (1958).

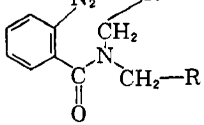
(12) L. G. Humber, H. Kondo, K. Kotera, S. Takagi, K. Takeda, W. I. Taylor, B. R. Thomas, Y. Tsuda, K. Tsukamoto, S. Uyeo, H. Yajima, and N. Yanaihara, *J. Chem. Soc.*, 4622 (1954).

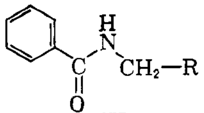
(13) A number of earlier claims have been disputed by Hey and Turpin.[8]

(14) For references to some recent examples, see H. B. Henbest, *Ann. Rep.*, 53, 144 (1956).

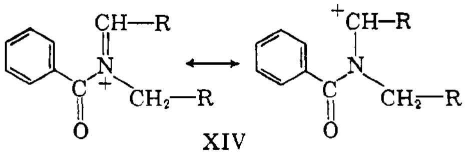
(15)(a) D. F. DeTar and T. Kosuge, *J. Am. Chem. Soc.*, 80, 6072 (1958); (b) H. Meerwein, H. Allendörfer, P. Beekman, F. Kunert, H. Morschel, F. Pawellek, and K. Wunderlich, *Angew. Chem.*, 70, 211 (1958).

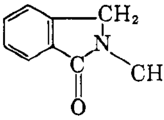
undergo the dealkylation reaction,[8,9] the replacement of this phenyl by an alkyl group, while simplifying the experimental procedures, was not expected to interfere with the dealkylation reaction. We have thus carried out the thermal decomposition in acid solution of the diazonium salts XIIa and XIIb prepared from the easily accessible compounds *o*-amino-*N*,*N*-dimethylbenzamide and *o*-amino-*N*,*N*-dibenzylbenzamide, respectively. In agreement with the hypothesis, XIIa produced formaldehyde, isolated as its dimedone derivative, and *N*-methylbenzamide (XIIIa) in the same yield (9.9%) while XIIb produced benzaldehyde, isolated as its 2,4-dinitrophenylhydrazone, and *N*-benzylbenzamide (XIIIb), again in comparable yields (17.7% and 14.7%, respectively). The higher yield of dealkylation products obtained in the dibenzyl case was expected on the basis of the stability of the presumed intermediate (XIVb) afforded by delocalization of the positive charge over the benzene ring. In both cases, phenols, arising by the more usual replacement of the nitrogen by the hydroxyl group of water, were the main products.


XII


XIII

a. R = H
b. R = C_6H_5


XIV


XV

In addition to these products, a fourth substance was isolated in the case of XIIa. This compound was eluted from alumina in the same fraction as XIIIa but could be separated cleanly from the latter by rechromatographing the mixture on a Florisil column. A clue to the identity of this material, m.p. 115–118°, was provided by an examination of its infrared spectrum which exhibited a carbonyl band at 1675 cm.$^{-1}$ As amides usually absorb at much lower frequencies unless a part of a five-membered ring, it appeared likely that the substance was a lactam. This was confirmed by the demonstration that the compound is *N*-methylphthalimidine (XV), identical with an authentic sample[16] prepared by reduction of *N*-methylphthalimide with zinc in hydrochloric acid.[17]

The formation of *N*-methylphthalimidine (XV) in this reaction is consistent with the proposed mechanism. Because of the proximity of the partially positive methylene carbon to the benzene ring, XIVa can undergo an internal electrophilic substitution to produce XV. This ring closure reaction must compete with the hydrolysis of XIVa which yields formaldehyde and *N*-methylbenzamide (XIIIa).[18]

1,5-Hydride transfers of the type proposed here are commonly encountered in the chemistry of medium size ring compounds.[20] In addition, several examples of nontransannular 1,5-hydride transfers have recently appeared in the literature. These include the acid-catalyzed conversion of 1-hydroxy-3,3-diphenyl-1H,3H-naphtho[1,8-c,d]pyran to 8-benzhydryl-1-naphthoic acid,[21] the reduction of a ketone by a carbinol amine in a degradation product of ajaconine,[22] the acid-catalyzed interconversion of normal and isosapogenins,[23] and the decomposition of 1,3,3-trimethylcyclohexyl hydroperoxide to a bicyclic ether induced by benzoyl chloride in pyridine.[24] The formation of tazettine upon methylation of haemanthidine[25] can also be nicely explained by a 1,5-hydride transfer. One of these examples[24] is especially analogous to our conversion of the diazonium salt (XIIa) to *N*-methylphthalimidine (XV) in that the hydride transfer is closely followed or concomitant with

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(16) G. Graebe and A. Pictet, *Ann.*, **247**, 302 (1888).

(17) We have re-examined the report by Graebe and Pictet[16] that *N*-methylphthalimidine (XV) forms in ether a hydrochloride of melting point, 120°, identical with the melting point of the free "base". We have confirmed the fact that such a precipitate is indeed formed when a saturated solution of hydrogen chloride in ether is added to an ethereal solution of XV. However, this precipitate was shown to be unchanged XV by infrared analysis. Similar behavior has been observed in this laboratory with another neutral compound; unpublished observations of Jack L. Pinkus.

(18) Abramovitch, Hey, and Long[19] have reported the isolation of a compound, m.p. 185°, from the decomposition of the diazonium salt derived from 1-amino-*N*-methyl-2-naphthanilide in addition to the product of demethylation, 2-naphthanilide. The elemental analysis and infrared spectrum of the 185° material are consistent with those expected for the compound that would be formed by hydride transfer, followed by electrophilic substitution of the positive methylene group into the naphthalene nucleus, in an analogous manner to the formation of *N*-methylphthalimidine (XV) from XIIa.

(19) R. Abramovitch, D. Hey, and R. Long, *J. Chem. Soc.*, 1781 (1957).

(20) V. Prelog, *Angew. Chem.*, **70**, 145 (1958); A. C. Cope, A. H. Keough, P. E. Peterson, H. E. Simmons, Jr., and G. W. Wood, *J. Am. Chem. Soc.*, **79**, 3900 (1957).

(21) R. L. Letsinger and P. T. Lansbury, *J. Am. Chem. Soc.*, **81**, 935 (1959).

(22) D. Dvornik and O. E. Edwards, *Proc. Chem. Soc.*, 280 (1958).

(23) R. B. Woodward, F. Sondheimer, and Y. Mazur, *J. Am. Chem. Soc.*, **80**, 6693 (1958).

(24) E. J. Corey and R. W. White, *J. Am. Chem. Soc.*, **80**, 6686 (1958).

(25) S. Uyeo, H. M. Fales, R. J. Highet, and W. C. Wildman, *J. Am. Chem. Soc.*, **80**, 2590 (1958).

the formation of a bond between the hydride donor and acceptor atoms.

A hydrogen *atom* transfer cannot be definitely excluded by these results, but a free radical decomposition of diazonium salts in strong acid solution seems considerably less likely than an ionic decomposition.[10] We are now seeking experimental evidence concerning this point.

EXPERIMENTAL[26]

o-Nitro-N,N-dimethylbenzamide. A mixture of 30 g. (180 mmoles) of Eastman *o*-nitrobenzoic acid, 24 g. (200 mmoles) of thionyl chloride, and 200 ml. of purified anhydrous dioxane[27] was heated on a steam bath with stirring until hydrogen chloride and sulfur dioxide were no longer evolved (*ca.* 2 hr.). The dioxane solution of the *o*-nitrobenzoyl chloride was added dropwise to a stirred solution containing 50 g. of 25% aqueous dimethylamine (12 g. of dimethylamine, 270 mmoles), 7.2 g. of sodium hydroxide, and 60 ml. of purified dioxane.[27] After the reaction mixture had cooled to within 20° of room temperature, the mixture was diluted to twice its original volume with water and extracted with four 50-ml. portions of methylene chloride. The extract was washed twice with water, dried over sodium sulfate, and evaporated to dryness. Upon cooling, the oily residue yielded a yellow solid. After drying this in a vacuum desiccator for 1 hr., there was obtained 31.2 g. (89% yield) of *o*-nitro-*N*,*N*-dimethylbenzamide, m.p. 77.2–78.0, reported[28] m.p. 78°.

o-Amino-N,N-dimethylbenzamide hydrochloride. A solution of 15 g. (77 mmoles) of *o*-nitro-*N*,*N*-dimethylbenzamide in 150 ml. of absolute ethyl alcohol was mixed with a small quantity of Raney nickel[29] and shaken in a Parr apparatus under 3 atm. of hydrogen for 3 hr. Hydrogen uptake was very slow after the first hour. The total pressure drop was 18.4 lbs. per sq. inch, calcd.: *ca.* 19.9 lbs. per sq. inch. Filtration from the catalyst and evaporation of the alcohol yielded 9.34 g. (80.3%) of light red oil.

The hydrochloride was prepared in benzene. After two recrystallizations from isopropyl alcohol, the compound partially decomposed at 190° but did not melt below 300°. The analytical sample was prepared by repeated recrystallizations from isopropyl alcohol.

Anal. Calcd. for $C_{19}H_{13}N_2OCl$: C, 53.86; H, 6.49; N, 13.96. Found: C, 54.17; H, 6.31; N, 14.47.

For structural proof, a small quantity of this hydrochloride was hydrolyzed by heating its solution in 6*N* sulfuric acid for 1 hr. on a steam bath. The solution was brought to cloudiness with dilute sodium hydroxide and extracted with three portions of ether. The extract was dried over sodium sulfate and evaporated. One recrystallization of the solid residue from hot water gave anthranilic acid, m.p. 143–144°, alone or mixed with an authentic sample.

Deamination of o-amino-N,N-dimethylbenzamide. A stirred solution of 2.00 g. (10 mmoles) of *o*-amino-*N*,*N*-dimethylbenzamide hydrochloride in 20 ml. of 3*N* sulfuric acid was cooled to 0° and treated dropwise with a saturated aqueous solution of sodium nitrite. The addition was continued until the reaction mixture gave an immediate blue color with starch-iodide paper. In order to destroy excess nitrous acid, urea was added until nitrogen evolution ceased. Decomposition of the diazonium salt commenced with nitrogen evolution when the reaction solution was warmed rapidly on a water bath to 50°. During a 1-hr. period, the temperature was gradually raised to 70°. Although nitrogen was no longer being visibly evolved, the reaction mixture was finally heated on a steam bath for 10 min. to insure complete decomposition. The solution was cooled in ice and extracted with eight 20-ml. portions of methylene chloride. The aqueous layer was treated with excess 10% alcoholic dimedone solution and allowed to remain overnight. Filtration yielded 280 mg. (9.9% yield) of adduct, m.p. 162–167°. After one recrystallization from ethanol, the solid weighed 191 mg., m.p. 186.5–188.5°, alone or mixed with an authentic sample of the dimedone adduct of formaldehyde.

The aqueous acidic filtrate, on treatment with base and chloroform extraction, yielded 50 mg. of unreacted *o*-amino-*N*,*N*-dimethylbenzamide.

The dried (Drierite) methylene chloride extract was concentrated under reduced pressure and the last traces of solvent were removed under a stream of nitrogen. The residue, a mixture of yellow solid and oil weighing 1.40 g., was dissolved in a minimum of hot benzene and cooled. The precipitate, m.p. 115–137°, after three recrystallizations from benzene, was still light yellow and weighed 330 mg., m.p. 164–166.5°. The infrared spectrum in chloroform exhibited characteristic absorption at 3150 cm.$^{-1}$ (O—H) and 1620 cm.$^{-1}$ (C═O). This was shown to be *N*,*N*-dimethylsalicylamide by hydrolysis of a portion in 12*N* sulfuric acid to salicylic acid, m.p. 154–155°, alone or mixed with an authentic sample. A further crop of 170 mg. of this amide was obtained from the chromatography (see below). The total yield of the phenolic product was therefore 30.3%. In previous runs, it had been ascertained that this compound cannot be separated from the nonphenolic products by alkaline extraction. This is probably due to strong internal hydrogen bonding between the phenolic hydrogen and the amide oxygen.

The combined mother liquors from the recrystallizations of the *N*,*N*-dimethylsalicylamide were concentrated and chromatographed on a column (2 × 56 cm.) containing 153 g. of Woelm alumina (neutral, activity grade No. 1). Elution with ether yielded 240 mg. of white solid, m.p. 45–101°. Elution with ethanol produced 173 mg. of crude *N*,*N*-dimethylsalicylamide, m.p. 147–157°. One recrystallization from benzene raised the m.p. to 154–157°. A portion (140 mg.) of the solid, m.p. 45–101°, was rechromatographed on Florisil (30 g.). Elution with benzene-ether (1:1) yielded 69 mg. of white solid, m.p. 69–79°. The melting point was raised to 77–80° by recrystallization from benzene–petroleum ether (b.p. 64–66°) and was undepressed when mixed with an authentic sample of *N*-methylbenzamide, whose preparation is described below. The infrared spectrum of this substance was also identical with that of the authentic sample. The overall yield of this compound was 9.9%. It was shown in control experiments that very little of this material is lost by hydrolysis in the 3*N* sulfuric acid. On further elution with the same benzene-ether solution, three fractions containing minute traces of oil were obtained followed by a number of fractions containing in all 65 mg. of white solid, m.p. 93–118°. Recrystallization from benzene–petroleum ether (b.p. 64–66°) gave colorless rhombic crystals, m.p. 115–118°. The mixture melting point with authentic *N*-methylphthalimidine, m.p. 112–114°, prepared as below, was 114–116°. The infrared spectrum of this compound which had a strong carbonyl peak at 1675 cm.$^{-1}$ in chloroform and 1685 cm.$^{-1}$ in carbon disulfide was identical with that of the authentic sample. Of the material placed on the Florisil column, 45% was thus *N*-methylphthalimidine. Of the 241 mg. of the mixture, m.p. 45–101°, obtained from the alumina column, 111 mg. was *N*-methylphthalimidine, representing an overall yield of 7.6%.

N-Methylphthalimidine (XV). A modification of the method of Graebe and Pictet[16] was used. A mixture of 3.00

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(26) Melting points were determined on a Kofler block unless the capillary method is specifically stated, in which case they are uncorrected. Infrared spectra were determined with a Perkin-Elmer model 21 spectrophotometer with sodium chloride optics. Microanalyses are by Mr. Otho Harris.

(27) A. Vogel, *Practical Organic Chemistry*, Longmans, Green and Co., London, 1951, p. 175.

(28) L. Van Scherpenzeel, *Rec. trav. chim.*, 20, 181 (1901).

(29) Ref. 27, p. 807.

g. (19 mmoles) of *N*-methylphthalimide[30] and 9.7 g. (149 mmoles) of zinc dust in 50 ml. of concd. hydrochloric acid was heated to reflux and then allowed to cool. The mixture of white precipitate and zinc was filtered, mixed with a small amount of water and filtered free of zinc. Sodium carbonate solution was added to the filtrate until a slight cloudiness appeared. The mixture was extracted with methylene chloride and the dried (sodium sulfate) extract was evaporated to yield 1.17 g. (42%) of pale yellow solid, m.p. 112–114° (lit.[30] m.p. 120°). Several recrystallizations from benzene–petroleum ether (b.p. 64–66°) failed to remove a slight quantity of persistent impurity. The infrared spectrum was identical to that reported by Theilacker and Schmidt.[31]

When an ether solution of hydrogen chloride was added to an ether solution of *N*-methylphthalimidine, an instant precipitate appeared,[16] m.p. 120–122°. The infrared spectrum of this compound was identical with that of *N*-methylphthalimidine itself. This treatment apparently removed the trace of impurity mentioned above.

N-Methylbenzamide (XIIIa). Benzoyl chloride was added dropwise to a solution prepared by dissolving methylamine hydrochloride and excess sodium hydroxide in water. The resulting solid, capillary m.p. 79–79.5° (lit.[32] m.p. 80°), was recovered unchanged after refluxing for 1 hr. in 3*N* sulfuric acid, conditions under which the diazonium salt decomposition was carried out.

o-Nitro-N,N-dibenzylbenzamide. A solution of *o*-nitrobenzoyl chloride, prepared as above, in purified dioxane was added dropwise to a mechanically stirred solution of 5.91 g. (30 mmoles) of dibenzylamine and 1.2 g. (30 mmoles) of sodium hydroxide in 60 ml. of dioxane. After the reaction heat had subsided, the mixture was diluted to twice its original volume with water and extracted with four portions of methylene chloride. The extract was washed twice with water to remove dioxane, dried over sodium sulfate, and evaporated. The residue, m.p. 80–89°, was recrystallized twice from ethanol to yield 6.0 g. (58% yield), capillary m.p. 104–105°.

o-Amino-N,N-dibenzylbenzamide. A mixture of 5.6 g. (16 mmoles) of *o*-nitro-*N*,*N*-dibenzylbenzamide, dissolved in 150 ml. of absolute ethanol, and a small quantity of Raney nickel was shaken in a hydrogen atmosphere for 4 hr. The decrease in hydrogen pressure was equal to that calculated for the reduction of the nitro group. Filtration of the nickel and evaporation of the alcohol produced 5.05 g. (99% yield) of crude product, m.p. 115–125°. The analytical sample was prepared by two recrystallizations from ethanol, capillary m.p. 131.5–132.5°.

Anal. Calcd. for $C_{21}H_{20}N_2O$: C, 79.70; H, 6.37; N, 8.85. Found: C, 79.83, 79.89; H, 6.67, 6.45; N, 8.92, 9.11.

Deamination of o-amino-N,N-dibenzylbenzamide. As this compound is insoluble in aqueous sulfuric acid, the diazotization was carried out in a medium of 2*N* sulfuric acid in acetic acid, prepared by diluting 27.8 ml. of concd. sulfuric acid to 500 ml. with glacial acetic acid. A solution of 1.28 g. (4.1 mmoles) of the amine in 20 ml. of this medium was cooled to 16° and diazotized by stepwise addition, with stirring, of solid sodium nitrite. The addition was stopped when 1 drop of reaction mixture turned starch-iodide paper an intense blue color. During the addition, the solution changed from colorless, through red, to greenblack. In order to decompose excess nitrous acid a small quantity of solid urea was added until nitrogen evolution ceased. The cold reaction mixture was diluted with water (19 ml.) until the first permanent cloudiness appeared, warmed to steam bath temperature, and heated for 1 hr. on the steam bath. At this time nitrogen was no longer being evolved. Upon cooling, a deep red oil separated. The mixture was made homogeneous by the addition of 23.5 ml. of 2*N* sulfuric acid in acetic acid. To a one quarter aliquot of this solution was added an excess of a saturated solution of 2,4-dinitrophenylhydrazine in acetic acid. After 5 hr., the precipitate was removed by filtration and dried. The solid weighed 52 mg., m.p. 235–239°, undepressed on admixture with an authentic sample of benzaldehyde-2,4-dinitrophenylhydrazone, m.p. 236–240°. The overall yield of benzaldehyde was thus 17.7%.

The remaining three quarters of the reaction mixture was dissolved in methylene chloride and extracted with four portions of 0.5*N* sodium hydroxide. (No acidic products could be obtained from this basic extract by acidification and ether extraction). The methylene chloride was dried over sodium sulfate and evaporated under reduced pressure. The red oily residue was dissolved in a minimum of benzene and adsorbed on an alumina column (2 × 20 cm., 126 g. of Fisher alumina). Elution with benzene-ether (3:2) produced 181 mg. of white solid, m.p. 60–80°. One recrystallization from benzene–petroleum ether (b.p. 64–66°) gave 95 mg. of white crystals, m.p. 104–105°, alone or mixed with an authentic sample of *N*-benzylbenzamide (XIIIb), prepared as below. The infrared spectrum was also identical with that of the authentic sample. This represents a 14.7% yield of *N*-benzylbenzamide in this deamination. The absence of acidic reaction products indicated that none of the *N*-benzylbenzamide was lost by hydrolysis during the reaction.

Further elution with ethanol-ether (1:1) produced 330 mg. of gum, which was not investigated further. Upon elution with ethanol-ether (5:1), 132 mg. of crude solid, m.p. 130–140°, was obtained. Three recrystallizations from alcohol brought the m.p. to 146–148°. This compound exhibits carbonyl absorption in the infrared spectrum at 1618 cm.$^{-1}$ (chloroform) and is very probably *N*,*N*-dibenzylsalicylamide, since it was hydrolyzed by heating in 12*N* sulfuric acid for 4 hr. to salicylic acid, m.p. 154–155°, alone or mixed with an authentic sample. The total yield of crude *N*,*N*-dibenzylsalicylamide was 13.6%.

N-Benzylbenzamide (XIIIb). A mixture of 4.9 g. (46 mmoles) of benzylamine, 2.44 g. (17 mmoles) of benzoyl chloride and 10 ml. of water in an Erlenmeyer flask was shaken vigorously during periodic addition of 10 ml. of 20% sodium hydroxide solution. The resulting solid was filtered, washed with water and dried. One recrystallization from benzene–petroleum ether (b.p. 64–66°) gave 2.8 g. (80%) of *N*-methylbenzamide as colorless needles, capillary m.p. 104–105.5° (lit.[33] m.p. 105–105.5°).

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