

## Mechanism of Benzidine and Semidine Rearrangements. Part XXIII.<sup>1</sup> Kinetics and Products of Acid-catalysed Conversion of 4-Phenyl-; 4-Nitro-; 2,2'-Diphenyl-; and 4,4'-Difluoro-substituted Hydrazobenzenes

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4-Phenyl-, 4-nitro-, and 2,2'-diphenyl-substituted hydrazobenzenes underwent rearrangements and concurrent disproportionations that were first order in substrate and second order in acid. The 4,4'-difluoro-compound also reacted first order in substrate but the order in acid rose from one to two with increasing acidity. These kinetic forms, the relative rates, and the nature of products could be rationalised by a polar transition-state mechanism that had been previously proposed.

THE kinetics and products of the acid and heat promoted rearrangements of several unsubstituted hydrazoarenes were successfully accounted for by a 'polar transition-state mechanism' whereas alternative mechanisms involving caged radicals or  $\pi$ -complexes could not accommodate the data.<sup>2</sup> Semi-quantitative analyses of the products of reduction of many substituted azobenzenes in acidic media under ill-defined conditions were also rationalised on the same basis. In parts XVI to XXII of this series we have put selected sets of the earlier data, which was gathered over fifty years ago,<sup>3</sup> on a quantitative footing and have shown that the revised findings are consistent in detail with the proposed mechanism. We now complete the re-investigation by studying the rearrangements and concurrent disproportionations of the compounds named in the title. Products of assumed but unproven structure have been recorded<sup>3</sup> for the reactions of 4-phenyl- and 2,2'-diphenyl-hydrazobenzenes but no rearrangement products have been characterised for nitro-substituted compounds, which appear to be appreciably stable to acids.<sup>4-8</sup> After the start of this work a quantitative study of the rearrangement of 4,4'-diphenyl-hydrazobenzene appeared.<sup>9</sup>

### RESULTS

All kinetic runs were carried out with perchloric acid as catalyst, 60% (v/v) dioxan-water as solvent and with the initial concentration of substrate *ca.*  $10^{-3}$ M. Except for those involving the 4-nitro-compound, all runs were carried out at an ionic strength ( $\mu$ ) buffered by the addition of lithium perchlorate. First-order rate constants,  $k_1$  (sec.<sup>-1</sup>), are for disappearance of substrate.

TABLE 1

|                                  |      |      |      |      |      |      |
|----------------------------------|------|------|------|------|------|------|
| $10^2[\text{H}^+]$ (M)           | 4.25 | 6.07 | 7.75 | 11.7 | 14.5 | 18.3 |
| $10^6 k_1$ (sec. <sup>-1</sup> ) | 12.8 | 21.4 | 31.3 | 60.4 | 93.4 | 13.6 |

4,4'-Difluorohydrazobenzene.—Rates at 25°,  $\mu$  0.2, are recorded in Table 1. A plot of  $\log k_1$  versus  $\log [\text{H}^+]$  was

<sup>1</sup> Part XXII, D. V. Banthorpe and M. O'Sullivan, *J. Chem. Soc. (B)*, 1968, 627.

<sup>2</sup> D. V. Banthorpe, E. D. Hughes, and C. K. Ingold, *J. Chem. Soc.*, 1964, 2864.

<sup>3</sup> P. Jacobsen, *Annalen*, 1922, **428**, 90.

<sup>4</sup> M. Dziurzynski, *Bull. Acad. Sci. Cracovie*, 1908, 400 (*Chem. Zentr.*, 1908, **11**, 948).

<sup>5</sup> G. Friebel and B. Rassow, *J. prakt. Chem.*, 1901, [2], **63**, 458.

curved with slopes 0.97 and 1.95 at 0.042 and 0.18M acid, but one of  $k_1/[\text{H}^+]$  versus  $[\text{H}^+]$  was linear indicating the kinetic form (1) where  $k_2$  is  $1.6 \times 10^{-3}$  sec.<sup>-1</sup> mole<sup>-1</sup> l and  $k_3$  is  $3.21 \times 10^{-2}$  sec.<sup>-1</sup> mole<sup>-2</sup> l<sup>2</sup>. Products, expressed as

$$k_1 = k_2[\text{H}^+] + k_3[\text{H}^+]^2 \quad (1)$$

percentage conversion of substrate, were 4,4'-difluoroazobenzene (40%), 4-fluoroaniline (40%), and 4,5'-difluoro-2'-aminodiphenylamine (18.5%; *o*-semidine linkage) at 0.1M-acid.

4-Phenylhydrazobenzene.—Rates at 0°,  $\mu$  0.6, are recorded in Table 2.  $H_0$  values are from references 10 and 11.

TABLE 2

|                                  |       |       |       |      |      |      |        |
|----------------------------------|-------|-------|-------|------|------|------|--------|
| $10^2[\text{H}^+]$ (M)           | 4.00  | 5.00  | 7.00  | 10.0 | 20.0 | 30.0 | 40.0   |
| $10^6 k_1$ (sec. <sup>-1</sup> ) | 0.243 | 0.313 | 0.574 | 1.37 | 5.92 | 12.5 | 22.5   |
| $10^2[\text{H}^+]$ (M)           | 60.0  | 80.0  | 100   | 200  | 300  | 400  | 600    |
| $H_0$                            |       |       | 1.86  | 1.55 | 1.36 | 1.22 | 1.02   |
| $10^6 k_1$ (sec. <sup>-1</sup> ) | 58.5  | 110   | 203   | 956  | 2510 | 4810 | 10,800 |

$\log k_1$  varied linearly with  $\log [\text{H}^+]$  or  $H_0$  in the ranges 0.004 to 0.10M and 0.10 to 0.60M acid with slopes  $2.06 \pm 0.04$  and  $2.10 \pm 0.05$  respectively. Products were: 4-amino-biphenyl (*ca.* 10%); aniline (*ca.* 10%); 4-phenylazobenzene (*ca.* 20%); 2,4'-diamino-5-phenylbiphenyl (*ca.* 30%); 2,4'-linkage of original substrate;  $R_F$  0.31 and 0.51 in hexane and cyclohexane systems, see Experimental section); and an uncharacterised *o*-semidine (*ca.* 20%;  $R_F$  0.42 and 0.61). The proportions of products as judged by the chromatographic pattern did not vary at 0.01, 1.0, and 1.0M acid and the proportion of azo-compound was 23, 20, and 21% at initial concentrations of substrate of 0.04, 0.078, and 0.0016M.

2,2'-Diphenylhydrazobenzene.—Rates at 0°,  $\mu$  1.00, are in Table 3.  $\log k_1$  varied linearly with  $H_0$  with a slope of  $2.0 \pm 0.10$ . Products were: 3,3'-diphenyl-4,4'-diaminobiphenyl (90%); 4,4'-linkage of substrate;  $R_F$  0.35 in cyclohexane system); 2-aminobiphenyl (5%;  $R_F$  0.85) and 2,2'-diphenylazobenzene (5%;  $R_F$  0.99) and were unaltered at 1.0 and 2.8M catalysing acid.

<sup>6</sup> D. D. Hartley and R. E. Lyons, *Proc. Indiana Acad. Sci.*, 1934, **44**, 124 (*Chem. Abs.*, 1936, **30**, 1778).

<sup>7</sup> A. G. Green and F. B. Rowe, *J. Chem. Soc.*, 1912, **101**, 2443.

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<sup>10</sup> D. V. Banthorpe, E. D. Hughes, C. K. Ingold, and J. Roy, *J. Chem. Soc.*, 1962, 3294.

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TABLE 3

|                                  |      |      |      |      |      |
|----------------------------------|------|------|------|------|------|
| $[H]^+(M)$                       | 0.80 | 1.00 | 1.21 | 1.31 | 1.59 |
| $H_0$                            | 0.87 | 0.75 | 0.50 | 0.40 | 0.11 |
| $10^5 k_1$ (sec. <sup>-1</sup> ) | 4.4  | 8.6  | 48.3 | 73.7 | 310  |

4-Nitrohydrazobenzene.—Rates at 0°, variable  $\mu$ , are in Table 4.  $\log k_1$  varied linearly with  $H_0$  with a slope of

TABLE 4

|                                  |      |      |      |      |
|----------------------------------|------|------|------|------|
| $[H]^+(M)$                       | 2.00 | 2.24 | 2.74 | 2.99 |
| $-H_0$                           | 0.26 | 0.50 | 0.90 | 1.10 |
| $10^5 k_1$ (sec. <sup>-1</sup> ) | 1.41 | 3.97 | 24.1 | 54.3 |

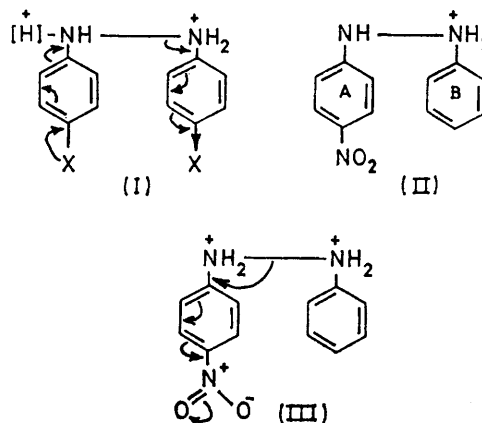
$2.0 \pm 0.05$ . Products were: aniline (10%;  $R_F$  0.89, formamide system); 4-nitroaniline (10%;  $R_F$  0.42); 4-nitroazobenzene (20%;  $R_F$  1.00); 4-amino-4'-nitrodiphenylamine (20%; *p*-semidine linkage;  $R_F$  0.46); unidentified, probably a diphenylene (*ca.* 25%; 2,4'-linkage of substrate;  $R_F$  0.80); tentatively identified (see Discussion), probably 2-amino-4'-nitrodiphenylamine (*ca.* 15%; *o*-semidine linkage;  $R_F$  0.57); unidentified, probably 2-amino-5-nitrodiphenylamine (trace; *o*-semidine linkage;  $R_F$  0.60). The proportions were unchanged at 2.0 and 3.0M catalysing acid.

## DISCUSSION

*Kinetics.*—We have suggested<sup>2,12,13</sup> that either sufficient electron release from a 2- or 4-substituent or a pronounced base-weakening effect of a 2-substituent could raise the one proton mechanism of rearrangement and its associated disproportionation [see equation (1)] to predominance over the route requiring two protons, in a reaction with a transition state in which the  $NN'$ -bond is largely broken and considerable charge is developed in the aniline-like moieties. Our present results fit into this picture.

A 4-phenyl substituent slightly weakens the basicity of aniline (aniline  $pK_a$  4.58; 4-aminobiphenyl  $pK_a$  4.30; all  $pK_a$  values are from ref. 14) and presumably similarly affects hydroazobenzene. Electron release from the substituent to the breaking  $NN'$ -bond in the transition state of rearrangement of the 4-phenyl compound apparently over-compensates for the reduction in rate compared with the parent hydrazobenzene caused by the lower basicity, but the overall increase is small (see Appendix) and the two-proton mechanism characteristic of the parent compound is followed. Introduction of a 4-phenyl group into the other ring introduces co-operative inductive and electromeric electron attractions [see (I; X = Ph) where the bracketed proton allows either the one or two-proton routes to be envisaged] and a one-proton route can intrude into the predominantly two-proton mechanism,<sup>9</sup> although the rate is not greatly altered. In contrast, although 2,2'-diphenylhydrazobenzene is undoubtedly less basic than hydrazobenzene (2-aminobiphenyl  $pK_a$  3.83),

neither this effect nor the presence of the substituents (whose electronic effects are now much reduced compared with the situation in the 4,4'-diphenyl isomer because of reduced conjugation between the aromatic rings due



to the presence of the imino-grouping) can evoke the one-proton route. The 2,2'-diphenyl isomer consequently reacts some 1000-fold slower than hydrazobenzene under comparable conditions.

A 4-fluoro-substituent in aniline hardly alters the basicity (4-fluoroaniline  $pK_a$  4.65) as inductive electron attraction causing base-weakening is balanced by mesomeric electron release that is greater than that shown by other halogens.<sup>15</sup> This electron release is more pronounced from the 4-position than from the 2-position<sup>15</sup> and the 4,4'-difluoro is unique amongst 4,4'-dihalohydrazobenzenes<sup>1,16,17</sup> in reacting concurrently by the one and two-proton routes at convenient acidities. The 2,2'-difluoro-compound is a weaker base (2-fluoroaniline  $pK_a$  3.20) but electron release from the substituent is not sufficient to elevate the one-proton route to importance:<sup>18</sup> in order to achieve the latter, 2-halogenosubstituents of greater base-weakening properties (*e.g.* 2-bromoaniline  $pK_a$  2.53; 2-iodoaniline  $pK_a$  2.60) have to be introduced.<sup>1,17</sup>

4-Nitrohydrazobenzene contains a strongly base-weakening substituent (4-nitroaniline  $pK_a$  1.0). Ion (II) must be formed in quantity comparable with that of the conjugate acid from hydrazobenzene but sufficient electron-release from the ring B is not available to act in concert with the electromeric effect of the nitro group and heterolytically to cleave the  $NN'$ -bond with the electrons moving away from the positive pole.  $NN'$ -Fission only occurs when the second (unfavourable) protonation has introduced adjacent-charge repulsion and the electronic shifts leading to the transition state can be represented as (III). The slowest known two-proton reaction results.

<sup>15</sup> C. K. Ingold, 'Structure and Mechanism in Organic Chemistry,' Bell, London, 1953, p. 722.

<sup>16</sup> D. V. Banthorpe and A. Cooper, *J. Chem. Soc. (B)*, 1968, 618.

<sup>17</sup> D. V. Banthorpe, C. K. Ingold, and M. O'Sullivan, *J. Chem. Soc. (B)*, 1968, 624.

<sup>18</sup> D. V. Banthorpe and M. O'Sullivan, *J. Chem. Soc. (B)*, 1968, 615.

<sup>12</sup> D. V. Banthorpe, A. Cooper, and C. K. Ingold, *J. Chem. Soc. (B)*, 1968, 609.

<sup>13</sup> D. V. Banthorpe, C. K. Ingold, and J. Roy, *J. Chem. Soc. (B)*, 1968, 64.

<sup>14</sup> D. D. Perrin, 'Dissociation Constants of Organic Bases in Aqueous Solution,' Butterworths, London, 1965.

Disproportionation to azo-compound and fission amines was considerable with all our substrates but the proportions of this pathway did not change at different concentrations of substrate or acid catalyst. Previous conclusions<sup>1,12</sup> that both rearrangement and disproportionation have a common rate-limiting step are thus reinforced.

*The Pattern of Substituent Effect on Rate.*—In the Appendix the available kinetic data for acid-catalysed conversions are compared. Uncertain extrapolations of the effects of temperature, solvent and ionic strength are necessary but the relative rates are probably accurate to  $\pm 0.3$  (quoted value). The overall pattern is of polar control, analogous to that discussed in the particular examples just considered and in agreement with the pattern previously deduced from semi-quantitative product data for the same reactions.<sup>2</sup>

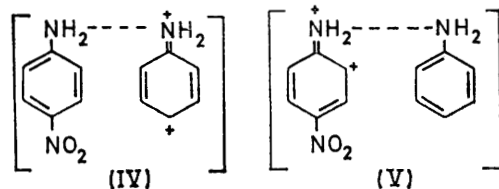
Detailed interpretation is blurred by complete ignorance of the  $pK_a$  values for the first and second protonations, for these must be known in order to dissect out the rate constants of the steps involving  $NN'$ -fission, although the previously used analogies with the  $pK_a$  values of correspondingly substituted anilines seem reasonable. Plots of  $(\log k_1 - pK_a')$  or  $(\log k_1 - pK_a' - pK_a'')$  for the results in the Appendix versus  $\sigma$  or  $\sigma^+$  values,<sup>19</sup> where the  $pK_a$  values refer to the anilines, give poor Hammett correlations with  $\rho$ ,  $-6.0 \pm 1.8$ . The kinetics of three ring-substituted  $NN'$ -dimethylhydrazobenzenes are stated<sup>20</sup> to correlate with  $\sigma^+$  values to give a  $\rho$ -value of  $-11.9$ . This unprecedentedly high value may merely reflect the paucity of the data.

We have failed to measure the  $pK_a$  values for mono-protonation of hydrazobenzene or its 2,2'-dichloro-derivative by either rapid observation of the u.v. spectra after mixing appropriate solutions or by an i.r. method.<sup>21</sup> Moreover, a claim<sup>22</sup> to have developed a novel method for this purpose is fallacious. The method was to react a mixture of the hydrazo-compound and a substituted aniline of known basicity with a limited quantity of acid in ether and to determine the composition of the precipitate containing the acid salts formed in competition. No account was, however, taken of relative solubilities or rates of precipitation and we have measured a difference in  $pK_a$  of ca. 5 for aniline and *N*-methyl-aniline using this technique; the accepted value is ca. 0.6!

*Products.*—On the basis of previously propounded rules<sup>2</sup> derived from the polar transition-state theory, 2,2'-diphenylhydrazobenzene should give 4,4'-linked products (numbering based on substrate) almost exclusively, and the 4,4'-difluoro- and 4,4'-diphenyl-compounds should give *o*-semidines accompanied by extensive disproportionation. These products are found. 4-Phenylhydrazobenzene also gives 2,4'- and probably 2,*N'*-linked products as expected for 4-sub-

stituted hydrazo-compounds with substituents capable of electromeric electron release coupled with inductive electron attraction.

4-Nitrohydrazobenzene should undergo electronic reorganisation as in (III) forming a transition state (IV) which leads to *N*,4'-; 2,4'; and (less favourably) *N*,2'-linked products. Unlike the anilino-moiety, the 'onium nitrogen cannot act as an electrophile; and the situation in (IV) in which the positive charges are anchored distant in the dication is more favoured than that in which the positive centre is at the *ortho*-position. *N*,4'- and 2,4'-linked compounds were indeed major rearrangement products and the *N*,2'-linked semidine



was tentatively identified. The latter behaved as expected of this class of compounds on chromatography, showed the appropriate colour reactions, and was reduced to a diaminodiphenylamine all of whose ring-hydrogens could be exchanged with deuterium under mild conditions. Another *o*-semidine, formed in traces was probably derived from the much less-favoured transition state (V). This *N'*-2-linked product would lead to a diaminodiphenylamine that would retain two ring-hydrogens per molecule under mild equilibration conditions but sufficient pure material could not be recovered to carry out the test.

#### APPENDIX

The available rate data are corrected<sup>23</sup> to standard conditions: solvent 60% dioxan-water at 25° and  $\mu$ , 1.0. Rate constants  $k_2$  and  $k_3$  are defined in equation (1). The units for constants calculated with Hammett's  $h_0$  function rather than with  $[\overset{\oplus}{H}]$  are the same, for  $h_0$  no less than  $[\overset{\oplus}{H}]$  is a concentration, but of a product ratio of the indicator and its derived ions used to establish the acidity scale. In general this concentration is determined by the concentration of  $[\overset{\oplus}{H}]$ , but is not equal to it. Literature sources are in ref. 24.

*Two Proton Mechanism* ( $R, R', 6 + \log k_3$ ): R and R' are the substituents in the two rings of hydrazobenzene: 4-Me, 4'-Me, 6.9; 2-Me, 2'-Me, 6.9; 2-MeO, —, 6.8; 4-Ph, —, 6.5; 3-MeO, 3'-MeO, 6.5; 4-Ph, 4'-Ph, 6.4; 4-Bu<sup>t</sup>, 4'-Bu<sup>t</sup>, 6.3; —, —, (hydrazobenzene) 6.2; 3-Me, 3'-Me, 6.2; 4-Cl, —, 5.9; 4-Bu<sup>t</sup>, 4'-Cl, 5.6;  $\alpha$ -naphthyl, —, 5.6; 4-I, 4'-I, 5.4; 4-Cl, 4'-Cl, 5.3; 4-Br, 4'-Br, 5.0; 2-F, 2'-F, 4.7;  $\beta$ -naphthyl, —, 4.5; 4-F, 4'-F, 4.5; 2-Br, 2'-Br, 2.8; 2-Ph, 2'-Ph, 2.5; 2-Cl, 2'-Cl, 2.2; 3-NO<sub>2</sub>, —, 0.9.

<sup>21</sup> W. Gordy, *J. Chem. Phys.*, 1941, **9**, 215.

<sup>22</sup> V. O. Lukashovich, *Russ. Chem. Rev.*, 1967, 895.

<sup>23</sup> A. Cooper, Ph.D. Thesis, University of London, 1966.

<sup>24</sup> D. V. Banthorpe, *Topics Carboxylic Chem.*, 1970, **1**, 1.

<sup>19</sup> P. R. Wells, 'Linear Free-Energy Relationships,' Academic Press, London and New York, 1968.

<sup>20</sup> W. N. White and E. E. Moore, *J. Amer. Chem. Soc.*, 1968, **90**, 526.

*One-Proton Mechanism* ( $R, R', 5 + \log k_2$ ).— $\alpha$ -Naphthyl,  $\alpha$ -naphthyl, 7·9; 2-MeO, 2'-MeO, 6·2;  $\beta$ -naphthyl,  $\beta$ -naphthyl, 6·1; 4-MeO, —, 5·8; 4-NHAc, —, 5·3; 4-CH<sub>2</sub>=CH, 4'-CH<sub>2</sub>=CH, 4·5;  $\alpha$ -naphthyl, —, 4·3; 2-MeO, —, 3·7;  $\beta$ -naphthyl, —, 2·6; 4-F, 4-F', 2·2; 2-Me, 2'-Me, 2·0; 3-NH<sub>2</sub>, 3' NH<sub>2</sub>, 1·5; 2-Br, 2'-Br, 0·9; 2-I, 2'-I, 0·7.

## EXPERIMENTAL

*Preparations.*—All substrates were recrystallised from ethanol or acetone and had satisfactory elemental analyses and melting points in agreement with literature values. U.v. spectra were measured with ether as solvent.

*2,2'-Diphenylhydrazobenzene:* 2,2'-Diphenylazobenzene (m.p. 144°;  $\lambda_{\max}$  466 nm,  $\epsilon$  432) was prepared<sup>25,26</sup> and reduced<sup>16</sup> to the hydrazo-compound: m.p. 185°. The latter was also formed by reduction of 2-nitrobiphenyl (50 g.) with sodium hydroxide (84 g.) in water (185 ml.), and methanol (500 ml.) under reflux for 10 hr.

*4-Phenylhydrazobenzene.*—4-Phenylazobenzene (m.p. 152°,  $\lambda_{\max}$  447 nm,  $\epsilon$  1056) was prepared by a method described for the 4-chloro-compound<sup>27</sup> and was reduced<sup>16</sup> to the hydrazo-compound, m.p. 126°.

*4-Nitrohydrazobenzene.*—4-Nitroazobenzene (m.p. 135°;  $\lambda_{\max}$  450 nm,  $\epsilon$  588) was prepared<sup>28</sup> and reduced<sup>29</sup> to the hydrazo-compound, m.p. 114°.

*4,4'-Difluorohydrazobenzene.*—4-Fluoroaniline was oxidised with manganese dioxide<sup>30</sup> to the azo compound, m.p. 99°, which was reduced<sup>16</sup> to the hydrazo-compound, m.p. 56°.

*Kinetic Methods.*—These have been described.<sup>1</sup> An excess of Bindschledler's Green was added to each aliquot from reactions of the 2,2'-diphenyl- and 4,4'-fluoro-compounds and back-titrated with titanous chloride. Rearrangement products of the other substrates slowly

reacted with the redox dye, and aliquots were quenched in 2M-sodium acetate and immediately titrated with Bindschledler's Green. Solutions of this titrant were made up *ca.* 2 hr. before use to enable the oxidising power to become constant.

*Product Analysis.*—Products were separated by paper chromatography<sup>1,10,12</sup> using formamide-impregnated paper and either cyclohexane or hexane as eluant. After development the compounds were recovered and compared spectroscopically with authentic samples. Semidines often were extensively oxidised both during reaction and recovery: these and certain diphenylines were not all available as standards and were tentatively identified on the basis of their u.v. spectra, characteristic chromatographic properties, and distinctive colour reactions on treatment with nitrous acid and coupling reagents.<sup>1</sup> In addition, 4,4'-diamino-3,3'-diphenylbiphenyl, for which no authentic preparative route has been reported, was assigned by its u.v. spectrum characteristic of a benzidine:  $\lambda_{\max}$  297 nm,  $\epsilon$  25,820; and by its n.m.r. spectrum.

The major of the two probable *o*-semidines formed by rearrangement of 4-nitrohydrazobenzene was reduced to a diaminodiphenylamine by treatment with zinc and ammonium chloride.<sup>16</sup> All ring hydrogens in the product were shown to be exchangeable for deuterium on heating at 50° for 10 hr. with deuterium chloride in deuterium oxide under air-free conditions.

*Miscellaneous.*—The  $pK_a$  for 4-acetoaminoaniline measured by an indicator method was 4·30.

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