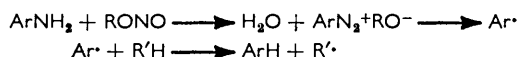


## A Simple and Convenient Deamination of Aromatic Amines

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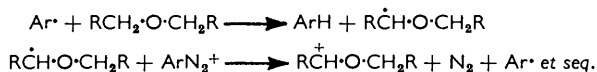
A simple, one-pot deamination of aromatic amines is described, consisting of aprotic diazotisation of the amine by pentyl nitrite in boiling tetrahydrofuran.

THE usefulness of alkyl nitrites as *in situ* diazotising agents has been demonstrated by the conversion of anthranilic acid into benzyne,<sup>1</sup> by a simple one-pot conversion of aniline and substituted anilines into the corresponding arynes,<sup>2</sup> and by conversion of arylamines into aryl radicals. The last reaction has been used to effect convenient aromatic arylations with arylamines<sup>3,4</sup> and acylarylamines,<sup>5</sup> thus replacing the Gomberg reaction, and to convert arylamines into aryl halides,<sup>4,6</sup> thus providing a convenient alternative to the Sandmeyer reaction. Since it has been shown that these reactions proceed *via* aryl radicals,<sup>6</sup> the extension of the *in situ* diazotisation method to deamination of arylamines by aryl-radical abstraction of hydrogen from a suitable solvent is an attractive possibility:



The patent literature contains one example of the realisation of this, wherein reaction of alkyl nitrite with a limited number of aromatic amines in *NN*-dimethylformamide led to deamination in unspecified yield.<sup>7</sup> This reaction is not of wide applicability, however, as a result of the inconvenience of using a large excess of such a high boiling solvent. We have now overcome this difficulty by using tetrahydrofuran as the hydrogen donor.

This compound was chosen as a result of the ease<sup>8</sup> with which C-H bonds  $\alpha$  to an ether linkage undergo abstraction reactions with aryl radicals derived in a redox fashion from aryldiazonium salts:



The reaction consists of the addition of the amine in tetrahydrofuran to an excess of pentyl nitrite in boiling tetrahydrofuran during 5 h. Standard work-up preceded by washing with sulphuric acid to remove pentyl alcohol in those cases where the product was of similar

b.p. led to the isolation of deaminated products summarised in the Table.

### Deamination of aromatic amines

ArNH <sub>2</sub>	ArH (%) yield	Identification*
2-NH <sub>2</sub> -Anthraquinone	65	M.p. 283—284° (lit., <sup>10</sup> 286°), m.s.
<i>o</i> -NH <sub>2</sub> ·C <sub>6</sub> H <sub>4</sub> ·SO <sub>2</sub> ·C <sub>6</sub> H <sub>4</sub> Cl( <i>p</i> )	89	M.p. 91—92° (lit., <sup>11</sup> 91—91·5°), m.s., n.m.r.
2,6-Br <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	87	M.s., n.m.r.
2,4,6-Br <sub>3</sub> C <sub>6</sub> H <sub>2</sub>	76	M.p. 121—122° (lit., <sup>10</sup> 121·5—122·5°), n.m.r.
2-NH <sub>2</sub> ·C <sub>6</sub> H <sub>4</sub> ·O·C <sub>6</sub> H <sub>3</sub> Me <sub>2</sub> (2,6)	76	M.p. 55—57° (lit., <sup>12</sup> 55—56°), m.s., n.m.r.
1-MeO,3-NO <sub>2</sub> ,4-NH <sub>2</sub> ·C <sub>6</sub> H <sub>3</sub>	71	N.m.r.
2-NH <sub>2</sub> -Fluorenone	66	M.s., i.r.
PhN=N·C <sub>6</sub> H <sub>4</sub> ·NH <sub>2</sub> ( <i>p</i> )	66	N.m.r.
<i>o</i> -NO <sub>2</sub> ·C <sub>6</sub> H <sub>4</sub> ·NH <sub>2</sub>	65	N.m.r., m.s.
2-NH <sub>2</sub> ·C <sub>6</sub> H <sub>4</sub> ·S·C <sub>6</sub> H <sub>2</sub> (OMe) <sub>3</sub> (2,4,6)	57	M.p. 124·5—125·5° (Found: C, 65·2; H, 5·8. C <sub>18</sub> H <sub>16</sub> O <sub>3</sub> S requires C, 65·0; H, 5·9%), m.s.
<i>o</i> -IC <sub>6</sub> H <sub>4</sub> ·NH <sub>2</sub>	37	N.m.r., m.s.
<i>p</i> -NH <sub>2</sub> ·C <sub>6</sub> H <sub>4</sub> ·CO <sub>2</sub> H	33	M.s.
<i>p</i> -NH <sub>2</sub> ·C <sub>6</sub> H <sub>4</sub> ·CHPh <sub>2</sub>	26	N.m.r., m.s.
<i>p</i> -HO·C <sub>6</sub> H <sub>4</sub> ·NH <sub>2</sub>	14	N.m.r.
2-NH <sub>2</sub> -Thiazole	16	N.m.r.
2,5-(MeO) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> ·NH <sub>2</sub>	12	N.m.r., m.s.†
2-Cl,6-MeC <sub>6</sub> H <sub>3</sub> ·NH <sub>2</sub>	0 ‡	
2-NH <sub>2</sub> -1-Me-Anthraquinone §	0	

\* Samples were compared with authentic specimens by the listed methods (m.s. = mass spectrum). † 2,5-Dimethoxynitrobenzene was also obtained. ‡ 7-Chloroindazole (55%), m.p. 134° (lit.,<sup>13</sup> 136·5—137·5°) was obtained (Found: C, 54·8; H, 3·1; N, 18·4. Calc. for C<sub>7</sub>H<sub>5</sub>ClN<sub>2</sub>: C, 55·1; H, 3·3; N, 18·4%). § 1*H*-Anthra[1,2-*c*]pyrazole-6,11-dione (24%), m.p. 264—265° (lit.,<sup>14</sup> 255—256°), correct m.s., and 2-methyl-1-nitroanthraquinone (4%), m.p. 265—269° (lit.,<sup>15</sup> 269—270°), correct m.s., were also found.

Dioxan may also be used instead of tetrahydrofuran should there be problems of solubility or excessive temperature stability of the intermediate diazonium system. In general diamines were not reduced satisfactorily, while 2-chloro-6-methylaniline and 2-methyl-1-aminoanthraquinone gave indazoles in varying amounts thus adumbrating a convenient alternative route to these compounds, based on the known formation of indazole from *o*-methylbenzenediazonium acetate.<sup>9</sup>

<sup>8</sup> D. B. Denney, N. E. Gersham, and A. Appelbaum, *J. Amer. Chem. Soc.*, 1964, **86**, 3180; J. I. G. Cadogan, R. M. Paton, and C. Thomson, *Chem. Comm.*, 1970, 229; C. Rüchardt and R. Werner, *Tetrahedron Letters*, 1969, 2407.

<sup>9</sup> R. Huisgen and H. Nakaten, *Annalen*, 1954, **586**, 84.

<sup>10</sup> 'Handbook of Chemistry and Physics, 46th edn.,' Chemical Rubber Co., 1965.

<sup>11</sup> C. Buehler and J. Masters, *J. Org. Chem.*, 1939, **4**, 262.

<sup>12</sup> A. Factor, H. Finkbeiner, R. A. Jerussi, and D. M. White, *J. Org. Chem.*, 1970, **35**, 57.

<sup>13</sup> G. H. Beaven, P. B. de la Mare, E. A. Johnson, and N. V. Klagen, *J. Chem. Soc.*, 1962, 988.

<sup>14</sup> J. Haworth and D. H. Hey, *J. Chem. Soc.*, 1940, 361.

<sup>15</sup> H. Römer and W. Link, *Ber.*, 1883, **16**, 697.

<sup>1</sup> L. Friedman and F. M. Logullo, *J. Amer. Chem. Soc.*, 1963, **85**, 1549.

<sup>2</sup> J. I. G. Cadogan, J. R. Mitchell, and J. T. Sharp, *Chem. Comm.*, 1971, 1; J. I. G. Cadogan, J. R. Mitchell, A. K. Robertson, and J. T. Sharp, *J.C.S. Perkin I*, 1972, 2563.

<sup>3</sup> J. I. G. Cadogan, *J. Chem. Soc.*, 1962, 4257.

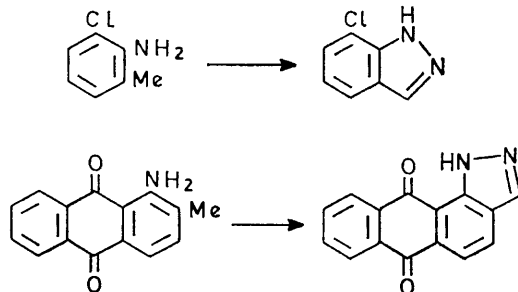
<sup>4</sup> Shu Huang, *Hua Hsieh Hsüeh Pao*, 1959, **25**, 171 (*Chem. Abs.*, 1960, **54**, 4489).

<sup>5</sup> E. B. McCall and E. J. Blackman, B.P. 929,093 (*Chem. Abs.*, 1963, **59**, 12,704).

<sup>6</sup> J. I. G. Cadogan, D. A. Roy, and D. M. Smith, *J. Chem. Soc. (C)*, 1966, 1249.

<sup>7</sup> W. Zerwck, M. Schubert, and R. Fleischhauer, G.P. 905,014 (*Chem. Abs.*, 1956, **50**, 12,111b).

The deamination reaction has several practical attractions: it is a one-pot reaction, it does not involve separate diazotisation, and work-up is simple.



#### EXPERIMENTAL

*General Procedure.*—The amine (15–20 mmol) in tetrahydrofuran (10–50 ml) was added dropwise during 1–2 h to a boiling solution of pentyl nitrite (1.5–2 mol. equiv.)

in tetrahydrofuran (30 ml). The solution was then boiled under reflux for a further 3 h. Removal of the solvent by rotary evaporation and of pentanol by distillation *in vacuo* left a residue. [Where appropriate, pentanol was removed by extraction of a solution of the residue in benzene with cold sulphuric acid (*d* 1.84).]

The products were isolated either by chromatography or by acid–base extractions, depending on their nature. The results are summarised in the Table. No attempts were made to optimise yields.

*Added in proof.* Since submission of this paper, an abstract of a dissertation [P. A. Vahjen, *Diss. Abs. (B)*, 1971, **32**, 2616] in which similar deaminations are reported has come to our attention.

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