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# ONE OF THE SIMPLEST METHODS FOR THE REPLACEMENT OF DIAZONIUM GROUPS BY HYDROGEN OR DEUTERIUM

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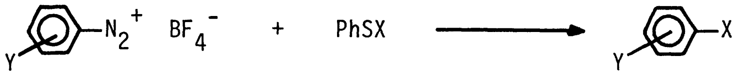
A simple and versatile method for the replacement of aromatic diazonium groups by hydrogen or deuterium was exploited by utilizing thiophenol as a reducing agent. The yields were over 84% for 14 examples and the isotopic purity was 100%. The reaction may involve a free radical mechanism.

The reduction of diazonium salts derived from aromatic primary amines has well been known to be a convenient method for the replacement of the amino group by hydrogen.

Although a great number of reducing agents have been known, they are not always effective to all types of aromatic diazonium salts,(1) and furthermore not applicable to the replacement by deuterium.(2)

We report here a new, simple, and efficient method utilizing thiophenol as a reducing agent to replace aromatic diazonium groups by hydrogen or deuterium (eq. 1).

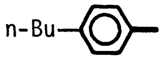
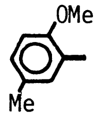
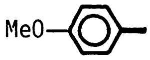
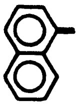
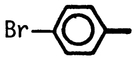
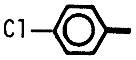
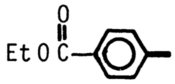
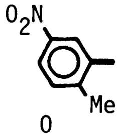
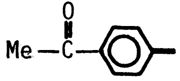
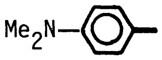
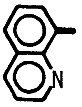
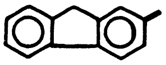
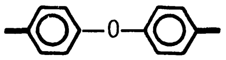
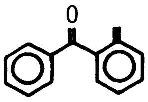


**1** **2** X = H or D ·························(1)

To a stirred suspension of aromatic diazonium tetrafluoroborates(3) (**1**, 1 mmol) in a mixture of water (10 ml) and pentane (1 ml) was added thiophenol (7 mmol) at room temperature. After stirring for 3 hrs, the reaction mixture was treated with potassium carbonate to remove unchanged thiophenol, and the usual working up gave the products (**2**) and diphenyl disulfide.(4) The replacement by deuterium was accomplished by using PhSD(5) and $D_2O$ instead of PhSH and water under an atmosphere of nitrogen. The results are shown in Table 1.

This method is superior to any other hitherto known method(1) in the following points. (1) Operation is the simplest. (2) Yields are always excellent. (3) None of the other substituents on the aromatic ring obstruct the replacement. (4) The isotopic

Table 1. Replacement of Diazonium Groups by Hydrogen or Deuterium

| Run | Ar- in $ArNH_2$ | $ArN_2BF_4$ Yield (%) | ArH Yield (%) | Isotopic Purity (%) of ArD[b] Measured by NMR Methods |
|---|---|---|---|---|
| 1. |  | 84 | 84 | ~100 |
| 2. |  | a | 92 | ~100 |
| 3. |  | a | 100 | ~100 |
| 4. |  | a | 100 | ~100 |
| 5. |  | a | 84 | ~100 |
| 6. |  | a | 85 | c |
| 7. |  | a | 88 | ~100 |
| 8. |  | 79 | 84 | ~100 |
| 9. |  | a | 95 | ~100 |
| 10. |  | a | 85 | ~100[d] |
| 11. |  | 95 | 92 | ~100 |
| 12. |  | 74 | 84 | ~100 |
| 13. |  | a | 97 | ~100 |
| 14. |  | 58 | 100 | ~100 |

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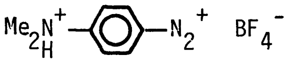
a. Footnote 7. b. The yields were the same as those of ArH.

c. The content of deuterium could not be determined since the nmr of *p*-chlorobenzene-$d_1$ did not show the spectrum with AA'BB' pattern.

d. The diazonium tetrafluoroborate was washed with $D_2O$ before it was reduced.

purity in the replacement by deuterium is excellent.

In the reduction of the diazonium salt prepared from *p*-dimethylaminoaniline (run 10), it is necessary to wash the salt with $D_2O$ prior to the reduction, since the diazonium salt is a protonated salt (**3**) and hence the presence of the proton gives the isotopic purity of only 50%.



**3**

In 1963, Price and Tsunawaki have reported the formation of a diazosulfide in some 50% yield in the reaction of a diazonium salt of *p*-nitroaniline with thiophenol under basic conditions.[6)] The reduction of **1** (Y = OMe, or $CO_2Me$) with thiophenol in aqueous sodium hydroxide, however, gave 10% of **2** (X = H) with many unidentified products. These results suggest us that our new reduction method is effective under neutral or acidic conditions.

Although it is not yet clear, the reaction pathway may be proposed as described in Scheme I, in which the reaction is initiated by the electron transfer between the diazonium salts and thiophenol to give $ArN_2\cdot$ and $PhS\cdot$, and aryl radicals ($Ar\cdot$) generated by the rapid decomposition of $ArN_2\cdot$ abstract a hydrogen from PhSH. In fact, diphenyl disulfide was obtained almost quantitatively along with ArH.

Scheme I

$$ArN_2^+\ BF_4^- \quad + \quad PhSH \xrightarrow{\qquad} ArN_2\cdot \quad + \quad PhS\cdot \quad + \quad HBF_4$$

$$ArN_2\cdot \xrightarrow{-\ N_2} Ar\cdot \xrightarrow[-\ PhS\cdot]{PhSH} ArH$$

$$2\ PhS\cdot \xrightarrow{\qquad} (PhS)_2$$

## References and Notes

1) (a) N. Kornblum, "Organic Reactions", Vol. II, John Wiley & Sons, Inc., New York (1944), p. 262; (b) N. Kornblum and D. C. Iffland, *J. Am. Chem. Soc.*, **71**, 2137 (1949); (c) N. Kornblum, G. D. Cooper, and J. E. Taylor, *ibid.*, **72**, 3013 (1950); (d) N. Kornblum, A. E. Kelley, and G. D. Cooper, *ibid.*, **74**, 3074 (1952); (e) W. J. Boyle, Jr., T. J. Broxton, and J. F. Bunnett, *J. Chem. Soc., Chem. Commun.*, **1971**, 1469; (f) J. I. G. Cadogan, D. A. Roy, and D. M. Smith, *J. Chem. Soc., (C)*, **1966**, 1249; (g) J. Nakayama, M. Yoshida, and O. Simamura, *Tetrahedron*, **26**, 4609 (1970); (h) J. I. G. Cadogan and G. A. Molina, *J. Chem. Soc., Perkin Trans. 1*, **1973**, 541; (i) Y. Hirose, G. H. Wahl, Jr., and H. Zallinger, *Helv. Chim. Acta*, **59**, 1427 (1976); (j) H. P. Doyle, J. F. Dellaria, Jr., B. Siegfried, and S. W. Bishop, *J. Org. Chem.*, **42**, 3494 (1977); (k) D. S. Wulfman, "The Chemistry of Diazonium and Diazo Groups", S. Patai, Ed., John Wiley & Sons, Inc., New York (1978), Part 1, p. 286.

2) D. V. Banthorpe and E. D. Hughes, *J. Chem. Soc.*, **1962**, 3314.

3) *p*-Carbethoxybenzenediazonium tetrafluoroborate and the other diazonium salts were prepared according to the methods described in (i) G. Shiemann and W. Winkelmüller, "Organic Syntheses", Collect. Vol. II, John Wiley & Sons, Inc., New York (1943), p. 299, and (ii) E. B. Starkey, "Organic Syntheses", Collect. Vol. II, John Wiley & Sons, Inc., New York (1943), p. 225, respectively.

4) The products were extracted with three 2 ml portions of ether and the combined ethereal solution was dried over magnesium sulfate. The solvent was evaporated and the products were isolated by distillation or by column chromatography.

5) PhSD is easily prepared by treating thiophenol with $D_2O$. In this reaction 3 mmol of PhSD gave satisfactory results.

6) C. C. Price and S. Tsunawaki, *J. Org. Chem.*, **28**, 1867 (1963).

7) The yields of diazonium salts were almost comparable to those shown in ref. 8.

8) A. Roe, "Organic Reactions", Vol. V, John Wiley & Sons, Inc., New York (1949), p. 193.

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