Reduction of Arenediazonium Fluoroborates to Arylhydrazines by Benzeneselenol

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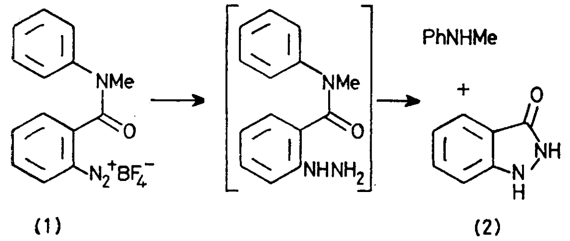
Summary Arenediazonium fluoroborates are converted in good yield into fluoroboric acid salts of arylhydrazines by benzeneselenol in methylene chloride; in methylene chloride-acetone, the reaction takes a different path, aryl phenyl selenides and arenes being the principal organic products.

Several methods have been reported for the reduction of arenediazonium cations to arylhydrazines,[1] but only two reagents, sodium sulphite and stannous chloride have found wide application; of these, only sodium sulphite seems to be of general utility, the stannous chloride method failing with some substituted benzenediazonium ions such as the *p*-nitro-derivative.

We report that when benzeneselenol is added to a suspension of benzenediazonium fluoroborate in refluxing methylene chloride, the solid is transformed into the fluoroboric acid salt of phenylhydrazine.† In a typical experiment,‡ the product, after washing with methylene chloride, was obtained in 80% yield. It showed no detectable diazonium i.r. absorption, was analytically pure, and was further characterised by conversion into benzaldehyde phenylhydrazone. The reduction appears to conform to the stoicheiometry shown in equation (1). No reaction was obtained in an experiment in which the selenol was replaced by benzenethiol.



$$[ArN_2]^+[BF_4]^- + 4PhSeH \rightarrow 2PhSeSePh + [ArNHNH_3]^+[BF_4]^- \qquad (1)$$

The transformation seems to be of some generality, since comparable yields of readily isolated hydrazinium salts were also obtained using *p*-chloro- and *p*-nitro-benzenediazonium fluoroborates.

When the diazonium salt (**1**) was subjected to the same experimental conditions, two major products, each obtained in *ca.* 70% yield, were *N*-methylaniline, and indazolone (**2**). Presumably these result from intramolecular hydrazinolysis of the amide bond.

The nature of the reaction with the benzenediazonium and *p*-chlorobenzenediazonium salts was greatly altered by the presence of *ca.* 5—10% acetone in the solvent. Added with the object of increasing the solubility of the diazonium salt, this led to copious nitrogen evolution when the selenol was introduced, and aryl phenyl selenides and arene were the major organic products.§ These products are to be expected if the diazonium ions are reduced to aryl radicals (Scheme).

$$ArN_2^+ + PhSeH \rightarrow Ar\cdot + N_2 + PhSe\cdot + H^+$$
$$Ar\cdot + PhSeH \rightarrow ArH + PhSe\cdot$$
$$2PhSe\cdot \rightarrow PhSeSePh$$
$$Ar\cdot + PhSeSePh \text{ (or } PhSe\cdot) \rightarrow ArSePh$$

SCHEME

The change in reaction pathway may be brought about by association between acetone and selenol in such a way as to alter the balance between the hydrogen-donor and electron-donor properties of the latter. Alternatively it is possible that the diazonium ions, and not the selenol, become solvated.[2]

Selenols are known to reduce sulphoxides to sulphides and disulphides to mercaptans apparently almost quantitatively.[3] The results presented here increase the scope of selenols as reducing agents to include a simple procedure for the synthesis of arylhydrazines, which are obtained in high yield and in convenient form for further handling.

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† Benzeneselenol was prepared as described in the literature (D. G. Foster, 'Organic Synthesis,' Coll. Vol. III, ed. E. C. Horning, Wiley, New York, 1955, p. 771), distilled under nitrogen, and subsequently handled by syringe techniques. Volatile organoselenium compounds are extremely toxic and should always be handled with appropriate precautions.

‡ PhSeH (*ca.* 2·0 g) was added to a suspension of $PhN_2^+ BF_4^-$ (0·58 g) in CH_2Cl_2 (25 ml) boiling under nitrogen. The mixture was heated to reflux for 2 h, cooled, and filtered. Diphenyl diselenide is recoverable from the filtrate.

§ Although the combined yield of these two products was high, their proportions varied with experimental conditions.

[1] I. G. Laing in Rodd's 'Chemistry of the Carbon Compounds,' 2nd edn., Vol. IIIc, ed. S. Coffey, Elsevier, Amsterdam, 1973, p. 59; for a general reduction using Ph_3P, see L. Horner and H. Stohr, *Chem. Ber.*, 1953, **86**, 1073.
[2] R. A. Bartsch, H. Chen, N. F. Haddock, and P. N. Juri, *J. Amer. Chem. Soc.*, 1976, **98**, 6753.
[3] W. H. H. Günther, *J. Org. Chem.*, 1966, **31**, 1202.