

## Oxidation of 1,1-Disubstituted Hydrazines to Tetrazenes with Benzeneseleninic Acid

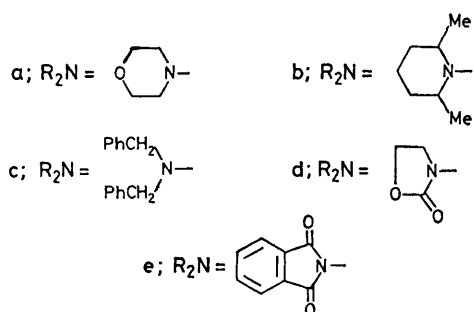
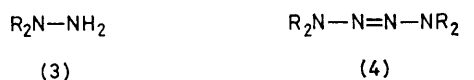
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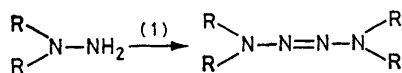
**Summary** The oxidation of 1,1-disubstituted hydrazines with benzeneseleninic acid in methanol affords the corresponding tetrazenes in high yield.

BENZENESELENINIC ACID (1) and anhydride (2) are valuable oxidizing agents which have recently found application in diverse synthetic transformations.<sup>1</sup> In particular, the oxidations of hydrazines and hydrazo-derivatives have

reacted more slowly and required treatment with (1) for 45 min at room temperature in the presence of an equimolar amount of sulphuric acid.† Products (4a) and (4b) were isolated by preparative thin layer chromatography while (4c–e) crystallized directly from the reaction mixture. This method therefore provides an especially convenient synthesis of tetrazenes.



been the subjects of several recent investigations.<sup>2</sup> To date, however, the reactions of (1) and (2) with 1,1-disubstituted hydrazines have not been explored, and the present communication describes preliminary results of such studies.



SCHEME

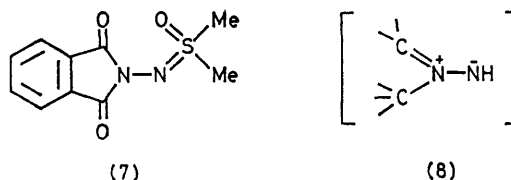
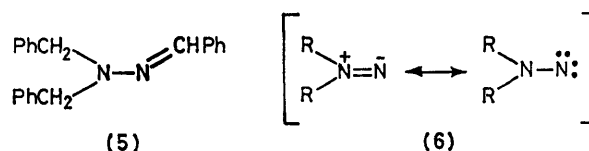
Thus, addition of (1) in a single portion to an equimolar amount of (3a–e) in methanol resulted in the formation of good to excellent yields of tetrazenes (4a–e) (see Scheme and Table). In the case of substrates (3a–d), the oxidation was vigorous and superior tetrazene yields were obtained when the reaction was performed at –10 °C and the mixture was worked up promptly. Hydrazone (3e)

TABLE. Preparation of tetrazenes (4).<sup>a</sup>

Hydrazine	Tetrazene	Isolated yield (%)
(3a)	(4a)	78
(3b)	(4b)	75
(3c)	(4c)	75
(3d)	trans-(4d)	96
(3e)	trans-(4e)	86

<sup>a</sup> The tetrazenes were identified by their m.p.s and by their i.r., u.v., and mass spectra.

Diphenyl diselenide was formed in all of the oxidations studied. Hydrazone (5) was a byproduct in the reaction of (3c) with (1) and was isolated in 22% yield. Bibenzyl, a frequent byproduct in the reaction of (3c) with other oxidants,<sup>3</sup> was not observed.



Aminonitrenes (6) are common intermediates in oxidations of 1,1-disubstituted hydrazines.<sup>4</sup> In order to test whether such species are implicated in the present reaction, an attempt was made to trap the aminonitrene derived from (3e) with dimethyl sulphoxide. The corresponding sulfoximine (7) was obtained in only 18% yield. This differs from the reported oxidation of (3e) with lead tetraacetate in dimethyl sulphoxide, where (7) was formed in

† In the absence of sulphuric acid, unchanged (3e) was recovered. It is not clear whether sulphuric acid actually catalyses the oxidation or merely increases the solubility of (3e). Compound (3d) was also oxidized in the form of its sulphate: oxidation of the free base was not attempted.

the much higher yield of 74%.<sup>5</sup> Furthermore, the tautomerization of aminonitrenes containing  $\alpha$ -hydrogens to species (8) is facilitated by protic solvents and often leads to the formation of products other than tetrazenes.<sup>6</sup> This contrasts with the present case where methanol provides a satisfactory medium for tetrazene formation in all of the examples listed in the Table. These results suggest

that intermediates other than aminonitrenes may be involved in the oxidation of 1,1-disubstituted hydrazines with benzeneseleninic acid.

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<sup>4</sup> T. L. Gilchrist and C. W. Rees in 'Carbenes, Nitrenes and Arynes,' Studies in Modern Chemistry, Thomas Nelson and Sons, London, 1969, pp. 36 and 97.

<sup>5</sup> D. J. Anderson, D. C. Horwell, E. Stanton, T. L. Gilchrist, and C. W. Rees, *J. Chem. Soc., Perkin Trans. 1*, 1972, 1317.

<sup>6</sup> D. M. Lemal and T. W. Rave, *J. Am. Chem. Soc.*, 1965, 87, 393; D. M. Lemal, F. Menger, and E. Coats, *ibid.*, 1964, 86, 2395.