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

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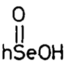
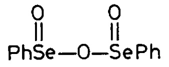
Summary The oxidation of 1,1-disubstituted hydrazines with benzeneseleninic acid in methanol affords the corresponding tetrazenes in high yield.

BENZENESELENINIC ACID (**1**) and anhydride (**2**) are valuable oxidizing agents which have recently found application in diverse synthetic transformations.[1] In particular, the oxidations of hydrazines and hydrazo-derivatives have been the subjects of several recent investigations.[2] 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.



$PhSe(=O)OH$

(1)



$PhSe(=O)-O-Se(=O)Ph$

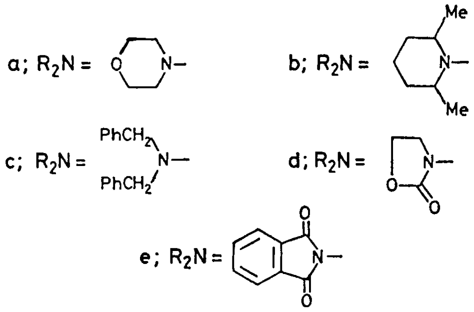
(2)

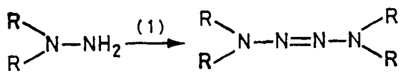
R_2N-NH_2

(3)

$R_2N-N=N-NR_2$

(4)





SCHEME

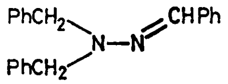
Thus, addition of (**1**) in a single portion to an equimolar amount of (**3a**—**e**) in methanol resulted in the formation of good to excellent yields of tetrazenes (**4a**—**e**) (see Scheme and Table). In the case of substrates (**3a**—**d**), the oxidation was vigorous and superior tetrazene yields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

TABLE. Preparation of tetrazenes (**4**).[a]

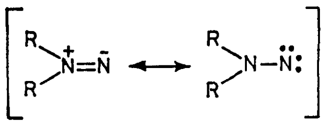
Hydrazine	Tetrazene	Isolated yield (%)
(**3a**)	(**4a**)	78
(**3b**)	(**4b**)	75
(**3c**)	(**4c**)	75
(**3d**)	*trans*-(**4d**)	96
(**3e**)	*trans*-(**4e**)	86

[a] The tetrazenes were identified by their m.p.s and by their i.r., u.v., and mass spectra.

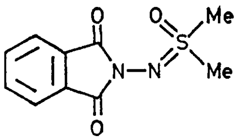
Diphenyl diselenide was formed in all of the oxidations studied. Hydrazone (**5**) was a byproduct in the reaction of (**3c**) with (**1**) and was isolated in 22% yield. Bibenzyl, a frequent byproduct in the reaction of (**3c**) with other oxidants,[3] was not observed.



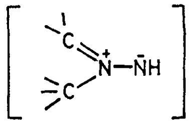
(5)



(6)



(7)



(8)

Aminonitrenes (**6**) are common intermediates in oxidations of 1,1-disubstituted hydrazines.[4] 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 sulphoximine (**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

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† 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%.[5] Furthermore, the tautomerization of aminonitrenes containing α-hydrogens to species (**8**) is facilitated by protic solvents and often leads to the formation of products other than tetrazenes.[6] 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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