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Oxidation of Amines with Diphenylseleninic Anhydride

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Summary Several primary amines have been oxidized in high yield to carbonyl compounds using diphenylseleninic anhydride.

To date, oxidations with (1) of amines which could form enamines (*e.g.*, 2-phenylethylamine and 1,2-diphenylethylamine) have led only to unrecognizable products.†

It has recently been demonstrated that PhSe(:O)OSe(:O)-Ph (1)¹ and PhSe(:O)Cl (2)² will undergo nucleophilic attack on Se (*e.g.* by an enolate anion), followed by spontaneous elimination of PhSeOH, to effect a net oxidation (*e.g.*, introduction of a double bond α to carbonyl³). We report here the application of the anhydride (1) to the oxidation, presumably by an analogous pathway, of primary amines, which in several cases leads to excellent yields of carbonyl compounds after hydrolytic workup (see Table). For example, treatment of a solution of 2-adamantylamine in CH₂Cl₂ with 1 equiv. of (1)⁴ for 24 h at room temp. afforded, after aqueous extraction and preparative t.l.c., a quantitative yield of adamantan-2-one.⁵ Treatment of benzylamine with 1 equiv. of (1) led to a mixture of benzaldehyde (isolated as benzoic acid) and benzonitrile; with 2 equiv. of (1), however, benzonitrile was obtained.

TABLE

Amine	Product	Yield (%) ^a
Ph ₂ CHNH ₂ ^b	Ph ₂ C=O	97(88)
Fluoren-9-ylamine ^b	Fluoren-9-one	98(84)
2-Adamantylamine ^b	Adamantan-2-one	100(91)
PhCH ₂ NH ₂ ^b	{ PhCO ₂ H	13(11)
	{ PhCN	26(—)
PhCH ₂ NH ₂ ^c	PhCN	96(—)

^a Isolated yields from preparative t.l.c.; yields in parentheses refer to product purified by sublimation or recrystallization. ^b With 1 equiv. of reagent (1). ^c With 2 equiv of (1).

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† Benzil has been identified as a minor product resulting from the reaction of (1) with 1,2-diphenylethylamine.

¹ D. H. R. Barton, P. D. Magnus, and M. N. Rosenfeld, *J.C.S. Chem. Comm.*, 1975, 301.

² H. J. Reich, J. M. Renga, and I. L. Reich, *J. Amer. Chem. Soc.*, 1975, 97, 5434.

³ Other methods for effecting this conversion involve a separate step for oxidation of an organoselenide: K. B. Sharpless, M. W. Young, and R. F. Lauer, *Tetrahedron Letters*, 1973, 1979; K. B. Sharpless, R. F. Lauer, and A. Y. Teranishi, *J. Amer. Chem. Soc.*, 1973, 95, 6137; H. J. Reich, I. L. Reich, and J. M. Renga, *ibid.*, p. 5813; D. L. J. Clive, *J.C.S. Chem. Comm.*, 1973, 695.

⁴ Prepared according to G. Ayrey, D. Barnard, and D. T. Woodbridge, *J. Chem. Soc.*, 1962, 2089.

⁵ A major by-product of these reactions is diphenyl diselenide (*cf.*, ref. 2 and D. L. Klayman and W. H. H. Günther, 'Organic Selenium Compounds,' p. 103, Wiley, New York, 1973).