

Conversion of Thiocarbonyl Compounds into Their Corresponding Oxo Derivatives using Benzeneseleninic Anhydride

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Summary A number of xanthates, thioesters, thiocarbonates, thioamides, and thiones have been converted into the parent oxo carbonyl derivatives in high yield by treatment with benzeneseleninic anhydride at room temperature in tetrahydrofuran.

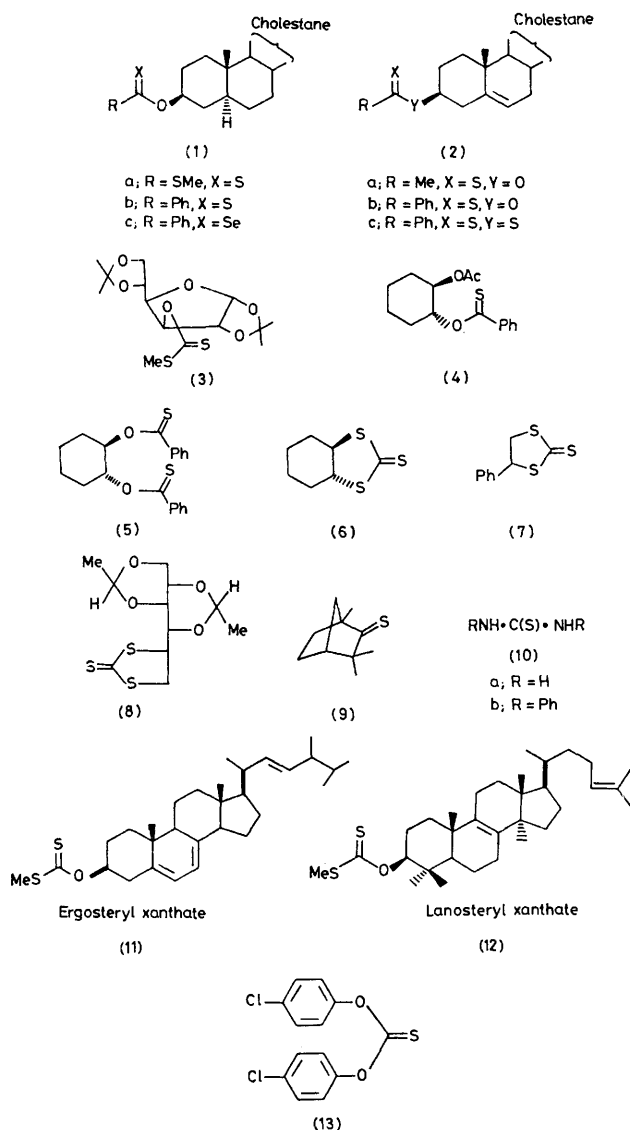
RECENTLY benzeneseleninic anhydride, $(\text{PhSeO})_2\text{O}$, has been shown to be a mild and versatile reagent for oxidation of organic substrates.¹ Here we report its use in the conversion of thiocarbonyl compounds into oxo derivatives, a reaction which has not received much attention in the literature.²

A variety of xanthates, thiocarbonates, thioamides, and thiones, (1)—(13), (Table), were treated at room temperature in tetrahydrofuran with 1 equiv. of benzeneseleninic anhydride. The reaction was routinely followed by t.l.c. and the products isolated by p.l.c. after disappearance of the starting material from the reaction mixture. In the

TABLE^a

Comp.	Reaction time/h	Yield of oxo-derivative /% ^b	Comp.	Reaction time/h	Yield of oxo-derivative /% ^b
(1a)	12	67	(6)	1	58
(1b)	3.5	69	(7)	3	84
(1c)	0.6	83	(8)	5	64
(2a)	4	59	(9)	2	89 ^c
(2b)	24	73	(10a)	3	60
(2c)	24	51	(10b)	5	39
(3)	2	75	(11)	2	71
(4)	2.5	62	(12)	1 ^d	63
(5)	2	88	(13)	4	70 ^e

^a Reactions were carried out with 1 equiv. of $(\text{PhSeO})_2\text{O}$ in tetrahydrofuran at room temperature unless stated otherwise. ^b Yields of products isolated by preparative layer chromatography unless stated otherwise. ^c Estimated by g.l.c. ^d Reaction carried out at reflux. ^e Isolated by precipitation and recrystallisation.



majority of examples the yields of carbonyl compounds were good. The major byproduct of the reaction was diphenyl diselenide which could be readily isolated and reoxidised to the anhydride. The examples were chosen to illustrate not only use in simple transformations but also in more complex natural products.

In several reactions we have compared the use of selenium dioxide as an alternative reagent for oxidation;³ however, only mixtures of products or very long reaction times were observed. The best of these reactions gave a 97% yield of benzoate after treatment of cholestan-3 β -ol selenobenzoate with SeO₂ for 3 days. We regard this result as a special case as generally the yields were much lower.

The fact that thiofenchone rapidly affords the oxo derivative is a good indication that reaction proceeds well even when there are considerable steric restrictions. Thio-camphor, on the other hand, gave three products on reaction with the anhydride which were characterised as camphor (9%), camphor quinone (54%), and 3-*endo*-phenylselenino-camphor (36%) which rapidly decomposes to camphor-quinone on standing at room temperature. In accord with this result, oxidation of an authentic sample of 3-phenyl seleno-camphor by *m*-chloroperbenzoic acid also afforded camphor-quinone at room temperature. Generally therefore, thiocarbonyl compounds which also contain an enolisable methylene group are expected to lead to more complex reaction mixtures on oxidation by the anhydride.

The precise mechanistic details of these reactions are not known although it is clear by n.m.r. spectroscopy that the oxo derivative is formed during the reaction even with strict exclusion of water and oxygen. Apart from diphenyl-diselenide as a reaction byproduct, we have also detected sulphur dioxide in the effluent gases.

The above reactions constitute a mild and effective method for the conversion of thiocarbonyl compounds into the corresponding oxo species.

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¹ D. H. R. Barton, D. J. Lester, and S. V. Ley, *J.C.S. Chem. Comm.*, 1977, 445 and references therein.

² R. Grashey, G. Schroll, and M. Weidner, *Chem.-Ztg.*, 1976, **100**, 496; M. Mikotajczyk and J. Luczak, *Synthesis*, 1975, 144; Y. Kinoshita, S. Kubota, S. Hashimoto, and H. Ishikawa, *Agric. and Biol. Chem. (Japan)*, 1973, **37**, 701; K. A. Petrov and L. N. Andreev, *Russ. Chem. Rev.*, 1971, **40**, 505; R. C. Forster, Ph.D. Thesis, University of London, 1977; F. Challenger, E. A. Mason, E. C. Holdsworth, and R. Emmott, *J. Chem. Soc.*, 1953, 292.

³ R. Boudet, *Bull. Soc. chim. France*, 1951, 846.