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REGIOSELECTIVE OXIDATION OF OLEFINS INTO α-PHENYLSELENO KETONES

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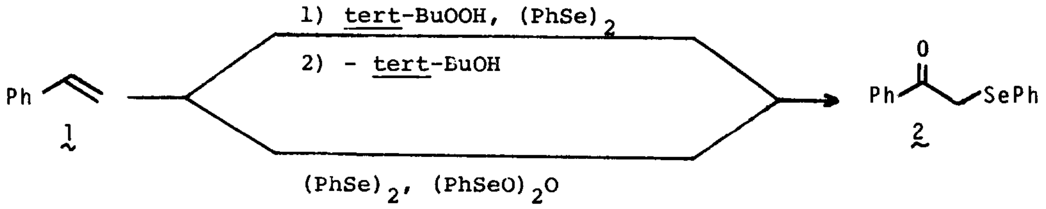
Recent studies have developed the efficient transformation of olefins to α-phenylseleno carbonyl compounds[1] which are potentially versatile synthetic intermediates and usually prepared via ketone or aldehyde equivalents.[2]

During exploration on the mechanistic point of view into the oxidation[1a] with diphenyl diselenide-bromine-hexabutyldistannoxane previously reported we have focused our attention to the generation and the reaction of a [PhSeOSePh] species[3] and now obtained an interesting result where such species may be working.

To generate diphenylselenenic anhydride **5**, diphenyl diselenide was treated with *tert*-BuOOH and the resulting *tert*-BuOH was removed from the reaction mixture. Styrene was oxidized to α-phenylselenoacetophenone **2** in the media prepared above. Further, treatment of styrene with a mixture (2:1 molar ratio) of diphenyl diselenide and diphenylseleninic anhydride **6**[4] also resulted in the formation of α-phenylselenoacetophenone, suggesting an analogous comproportionation to Sharpless and Reich's observations.[5]



(1)

$$\underset{\mathbf{3}}{(\mathrm{PhSe})_2} + \underset{\mathbf{4}}{\textit{tert}\text{-BuOOH}} \longrightarrow \underset{\mathbf{5}}{[\mathrm{PhSeOSePh}]} + \textit{tert}\text{-BuOH} \qquad (2)$$

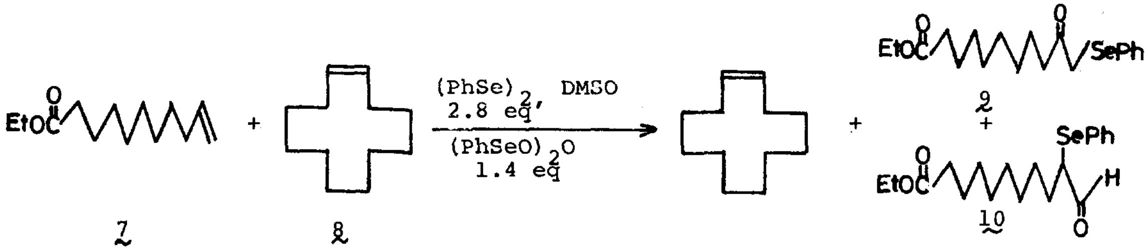
$$2\,(\mathrm{PhSe})_2 + \underset{\mathbf{6}}{(\mathrm{PhSeO})_2\mathrm{O}} \rightleftarrows 3\,[\mathrm{PhSeOSePh}] \qquad (3)$$

In comparison with the previous result[1a], the present reaction need a slightly higher reaction temperature. However an easy procedure without rather laborious work-up for the removal of the stanne moiety led us to further examinations into the possibility for organic synthesis.

Thus regioselectivity on the oxidation of terminal olefins[6] and allylic alcohols was studied. In acetonitrile 1-decene was converted to a ca. 1:1 mixture of 2-phenylseleno aldehyde and 1-phenylseleno ketone but in other solvents (toluene, sulfolane, etc.) the former predominated. The use of DMSO improved the products distribution remarkably e.g., usually 1-phenylseleno ketones were obtained in 90--95% regioselectivity. However the heterogeneous nature of the terminal olefins studied here and DMSO prevented smooth conversion of the starting materials and almost 4 equivalent of reagents must be employed for reproducible results.[7] Those results were summarized briefly in Table I.

Another interesting feature was observed in the oxidation of allylic alcohol derivatives. While allyl acetates, benzoates, or pivarates did not afford satisfactory preference for regioselectivity, benzyl ethers showed the introduction of carbonyl functionality into the remote sp_2 carbon from the hydroxy group with high regioselectivity. The steric congestion around the double bond appear to account for this observation.[8] In addition bis-benzyl ether of type ($PhCH_2OCH_2CH=CHCH_2OCH_2Ph$) was also oxidized to the α-phenylseleno ketone in good yield.

Furthermore the difference of the reactivities between terminal olefins and internal ones was demonstrated in the following example;



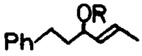
7 1.0 eq   8 1.0 eq   >90% recovery   64% (9/10=93/7)

In summary, the present oxidation appears to involve an addition process of a [PhSeOSePh] species to olefins, giving directly α-phenylseleno carbonyl compounds in good yields.[9]

The generalities of this procedure both on terminal and internal olefins make a feasible consideration of double bonds as convenient sources for α-phenylseleno ketones. Moreover regioselectivities found in terminal and allyl benzyl ethers should also be worth mentioning.

Works on extending to the oxidation of allylic and homoallylic alcohol derivatives are currently in progress.

Table I. Oxidation of Olefins to α-Phenylseleno Carbonyl Compounds.[a]

Olefin	Solvent	Method	Products[b] (ratio)	% yield[c]
Styrene	CCl_4	A	$PhCOCH_2SePh$	87
1-Decene	$C_6H_5CH_3$	A	$C_8H_{17}COCH_2SePh$, $C_8H_{17}CH(SePh)CHO$ (66:34)	81
	CH_3CN	B	(54:46)	72
	$DMSO-C_6H_5CH_3$ (1:1)	B	(86:10)	86
	DMSO[d,e]	A	(91:9)	70
1-Dodecene	DMSO[d,e]	A	$C_{10}H_{21}COCHSePh$, $C_{10}H_{21}CH(SePh)CHO$ (93:7)	71
Ethyl 10-undecenoate	DMSO[d,e]	A	9, 10 (94:6)	70
Cyclododecene	$C_6H_5CH_3$[d]	A	$\underbrace{C_{10}H_{20}COCH}SePh$	67[f]
Cinnamyl acetate	C_6H_6[d]	A	PhCOCH (SePh)CH_2OAc	83
 R=$PhCH_2$	C_6H_6[d]	A	11, 12 (95:5)	79
R=Ac	$C_6H_5CH_3$[d]	A	(66:34)	58
 R=$PhCH_2$	C_6H_6[d]	A	$ROCH_2COCH(SePh)CH_2OR$	81

[a] Reactions were carried out in 0.5--1.0 mmol in a refluxing solvent with a reactant ratio; olefin:$(PhSe)_2$:tert-BuOOH = 1.0:2.0:2.0 or Olefin:$(PhSe)_2$:$(PhSeO)_2O$ = 1.0:1.4:0.7 unless otherwise cited. Reaction periods were 0.5--7 hours. [b] All compounds were characterized either by direct comparison with the authentic samples[1a] or spectroscopic and elemental analyses.
[c] Isolated yield. [d] Olefin:$(PhSe)_2$:tert-BuOOH = 1.0:4.4:4.4. [e] The reaction was carried out at 110 °C. [f] 2-Cyclododecenone (ca. 15%) was formed.

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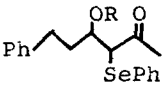

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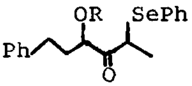

A typical procedure follows;

α-Phenylselenoacetophenone (method A).

To a solution of diphenyl diselenide (624 mg, 2.0 mmol) in 5 ml of carbon tetrachloride were added 2 g of molecular sieves (3A) and a solution of 70% tert-BuOOH (256 mg, 2.0 mmol) in 5 ml of carbon tetrachloride and the mixture was refluxed for 1 hr. Then all the solvent as well as tert-BuOH was removed and a solution of styrene (104 mg, 1.0 mmol) in 5 ml of carbon tetrachloride was added to the resulting pale yellow solid.[10] After stirring for an hour under reflux, the reaction mixture was washed with sat. aqueous NaCl and dried ($MgSO_4$). Concentration of the solvent gave a brown oil, which was purified on silica gel column chromatography to give the title compound (238 mg, 87%) and diphenyl diselenide (414 mg).

(Method B)

To a solution of diphenyl diselenide (437 mg, 1.4 mmol) and diphenylseleninic anhydride (252 mg, 0.7 mmol) in 5 ml of the solvent were added an olefin (1 mmol) in 5 ml of the solvent and 2 g of molecular sieves (3A), and the mixture was stirred under reflux until the starting olefin was all comsumed. The resulting reaction mixture was worked up and purified as indicated above.

References and Notes

1. (a) I. Kuwajima and M. Shimizu, Tetrahedron Lett., 1277 (1978); (b) T. Takahashi, H. Nagashima, and J. Tsuji, Tetrahedron Lett., 799 (1978); (c) S. Raucher Tetrahedron Lett., 2261 (1978).
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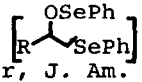
3. A possibility for the formation of this species was cited, see ref 4a and 5.
4. (a) G. Ayrey, D. Barnard and D. T. Woodbridge, J. Chem. Soc., 2089 (1962); (b) D. H. Barton, P. D. Magnus, and N. Rosenfeld, J. Chem. Soc., Chem. Commun., 301 (1975).
5. (a) T. Hori and K. B. Sharpless, J. Org. Chem., 43, 1689 (1978); (b) H. J. Reich, S. Wollowitz, J. E. Trend, F. Chow, and D. F. Wendelborn, J. Org. Chem., 43, 1697 (1978).
6. On the regioselectivity of PhSeBr addition to terminal olefins, see S. Raucher, J. Org. Chem., 42, 2950 (1977); Tetrahedron Lett., 3909 (1977).
7. The use of molecular sieves (3A) is required for reproducible yields especially in DMSO solution.
8. W. H. Putterbauch and M. S. Newman, J. Am. Chem. Soc., 79, 3469 (1957); D. R. Dalton, V. P. Dutta, and D. C. Jones, J. Am. Chem. Soc., 90, 5498 (1968).
9. A possible intermediate  may collapse to ketone, see K. B. Sharpless and R. F. Laner, J. Am. Chem. Soc., 94, 7154 (1972).
10. In the case of DMSO as solvent, the olefin was directly introduced, and the addition of DMSO was followed.

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