Tetrahedron Letters No. 15, pp 1277 - 1280, 1978. Pergamon Press. Printed in Great Britain.

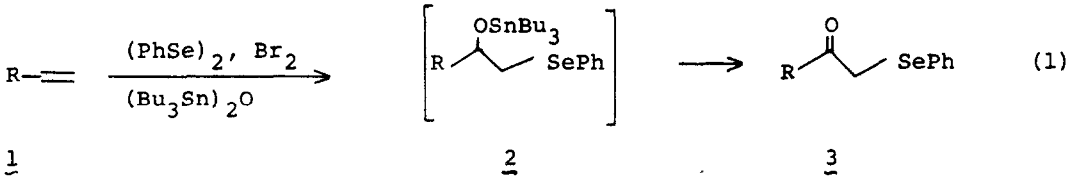
OXIDATION OF OLEFINS WITH DIPHENYL DISELENIDE-BROMINE-HEXABUTYLDISTANNOXANE. A ONE-STEP PREPARATION OF α-PHENYLSELENO CARBONYL COMPOUNDS FROM OLEFINS.

Isao Kuwajima* and Makoto Shimizu
Department of Chemistry, Tokyo Institute of Technology
Ookayama, Meguro-ku, Tokyo 152

(Received in Japan 23 January 1978; received in UK for publication 21 February 1978)

For oxidation of olefins to the corresponding α-functionalized carbonyl compounds, one-step procedures have eliminated some drawbacks and provide easy and simple approaches to them.[1] Much interest in α-seleno carbonyl compounds due to their versatility in synthetic organic chemistry[2] led us to explore an easy synthesis of them from olefins. Recently trialkyltin alkoxides are often and efficiently employed in oxidation of alcohols.[3] On the other hand, species such as PhSeX(X = Cl, Br,OAc, $OCOCF_3$) are well known to undergo electrophilic trans-1,2-addition to olefins or acetylenes.[4]

Bearing such phenomena in mind, we have utilized diphenyl diselenide, bromine and hexabutyldistannoxane under the expectation that these reagents would produce $PhSeOSnBu_3$, a hitherto unknown species, and that it would undergo addition reaction with olefins.



We have found that this procedure is an effective way for the preparation of α-phenylseleno carbonyl compounds directly from olefins.

A typical procedure under the optimum conditions is given below. To a solution of diphenyl diselenide (686 mg, 2.2 mmol) and hexabutyldistannoxane (1311 mg, 2.2 mmol) in 3 ml of chloroform[5] were added a carbon tetrachloride solution of bromine (1.55 ml, 1.35 M, 2.10 mmol) and then a solution of styrene (104 mg, 1.0 mmol) in 2 ml of chloroform. After stirring for 2 hr under reflux, the brown mixture was washed with 5% aqueous $Na_2S_2O_3$, 5% aqueous NaOH, and satd. aqueous NaCl. The crude mixture was dried ($MgSO_4$), concentrated, and purified on silica gel column chromatography[6] followed by simple distillation to afford α-phenylselenoacetophenone (204 mg, 74%) and recovered diphenyl diselenide (369 mg).

The use of one equivalent or lesser amount of diphenyl diselenide resulted in decrease in product yields (<60%). Examination of the results shown in Table I reveals that this reaction possesses satisfactory generality. In general internal olefins were less reactive than terminal ones and excess amounts of reagents were needed for completion of the reaction. Terminal olefins except for styrene usually afforded a mixture of α-phenylseleno ketone and aldehyde, where the former predominated. However, the ratio could be improved to a certain extent by varing the solvent. For example, in oxidation of 1-decene, a 80:20 ratio of the α-phenylseleno ketone to the aldehyde was obtained (56% yield) when benzene was used as solvent, whereas it was 58:42 (60%) in THF solution. In strong contrast to other PhSeX analogues,[4] the present reaction gave no adduct with vinyl bromides or α,β-unsaturated ketones. As solvent ordinary aprotic solvents may be employable and only their boiling points appear to be crucial for the reaction.

Although direct evidence of such species as 4 has not been obtained yet, the following observations may support the involvement of an intermediate 2, derived from the reaction of 4 with an olefin. First, an addition of phenylselenenyl bromide to hexabutyldistannoxane made rapid disappearance of the dark brown color of phenylselenenyl bromide together with the formation of diphenyl diselenide, which suggests the presence of the following equilibrium.

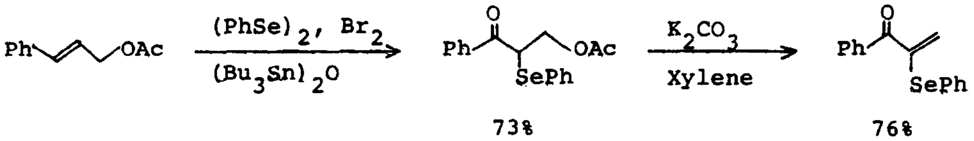
In addition, we have attested that **6** which was considered to be formed on treatment of hexabutyldistannoxane with bromine[3b] does not add to olefins under a variety of conditions (even in the presence of a radical initiator).

$$(Bu_3Sn)_2O \xrightarrow{PhSeBr} \underset{\mathbf{4}}{Bu_3SnOSePh} + \underset{\mathbf{5}}{Bu_3SnBr}$$

$$\underset{\longleftarrow}{\xrightarrow{PhSeBr}} (PhSe)_2 + \underset{\mathbf{6}}{Bu_3SnOBr} + 2\ Bu_3SnBr \qquad (2)$$

Secondly, when the reaction was carried out at low temperatures (0 °C--room temp) or in the case of α-methylstyrene, β-hydroxy selenides were obtained after aqueous workup, suggesting the involvement of an intermediate **2**.

Further, cinnamyl acetate was converted to α-phenylselenoenone in good yield, demonstrating another approach to this type of compounds.[7]



(3)

Thus the present method offers an easy one-step transformation of olefins to α-phenylseleno carbonyl compounds and further studies on the selectivity in the oxidation of terminal olefins are now in progress.

Table I. Oxidation of Olefins with Diphenyl Diselenide- Bromine-Hexabutyldistannoxane.[a]

Olefin	Solv.	Products[b] (ratio)	Yield,[c] %
Styrene	$CHCl_3$	$PhCOCH_2SePh$	74
1-Decene	CCl_4	$C_8H_{17}COCH_2SePh$, $C_8H_{17}CH(SePh)CHO$ (68:32)	68
Ethyl 10-undecenoate	CCl_4	$EtOCOC_8H_{16}COCH_2SePh$, $EtOCOC_8H_{16}CH(SePh)CHO$ (77:23)	60
Cinnamyl acetate[d]	$C_6H_5CH_3$	$PhCOCH(SePh)CH_2OAc$	73
Cyclooctene[d]	$C_6H_5CH_3$	$\underline{C_6H_{12}COCH}SePh$	72[e]
Cyclododecene[d,f]	C_6H_6	$\underline{C_{10}H_{20}COCH}SePh$[g]	52
α-Methylstyrene	CCl_4	$PhCCH_3(OH)CH_2SePh$	62

[a] Reactions were carried out in 1 mmol scale in a refluxing solvent, with a reactant ratio : olefin : $(PhSe)_2$: Br_2 : $(Bu_3Sn)_2O$ = 1.0:2.2:2.1:2.2. Reaction periods were 2-7 hours. [b] All compounds were fully characterized by IR, NMR, and mass spectroscopy. [c] Isolated yield. [d] Olefin : $(PhSe)_2$: Br_2: $(Bu_3Sn)_2O$ = 1.0:4.4:4.2:4.4. [e] Yield determined by NMR. [f] A mixture of (E) and (Z) isomers. [g] 2-Cyclododecenone (ca. 20%) was formed.[8]

References and Notes

1. (a) G. Cardillo and M. Shimizu, J. Org. Chem., in press; (b) K. B. Sharpless, A. Y. Teranishi, and J.-E. Bäckvall, J. Am. Chem. Soc., 99, 3120 (1977); K. B. Sharpless and A. Y. Teranishi, J. Org. Chem., 38, 185 (1973); (c) B. W. Ponder and D. R. Walker, ibid., 32, 4136 (1967).
2. H. J. Reich, J. M. Renga, I. L. Reich, J. Am. Chem. Soc., 97, 5434 (1975), and references cited therein.
3. (a) K. Saigo, A. Morikawa, and T. Mukaiyama, Bull. Chem. Soc. Jpn., 49, 1656 (1976), Chem. Lett., 145 (1975); (b) Y. Ueno and M. Okawara, Tetrahedron Lett., 4597 (1976); (c) T. Ogawa and M. Matsui, J. Am. Chem. Soc., 98, 1629 (1976); (d) J. C. Pommier and D. Chevolleau, J. Organometal. Chem., 74, 405 (1974).
4. (a) H. J. Reich, J. Org. Chem., 39, 428 (1974); (b) K. B. Sharpless and R. F. Lauer, ibid., 39, 429 (1974); (c) S. Raucher, ibid., 42, 2960 (1977), and references cited therein.
5. In certain cases product yields were raised when the reaction was carried out in the presence of 3A molecular sieves.
6. Ammonium fluoride can also be used for removal of Bu_3SnBr, see ref. 3a.
7. H. J. Reich and S. K. Shah, J. Am. Chem. Soc., 99, 263 (1977).
8. $(Bu_3Sn)_2O$-Br_2 oxidizes sulfides to sulfoxides, Y. Ueno, T. Inoue, and M. Okawara, Tetrahedron Lett., 2413 (1977).