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THE REGIOSPECIFIC SYNTHESIS OF α-PHENYLSELENO KETONES FROM MONOSUBSTITUTED ALKENES.[1]

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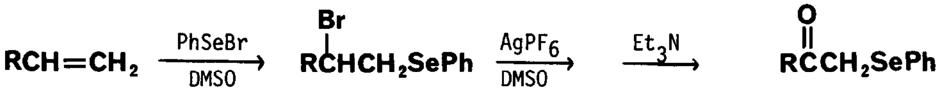
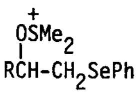
α-Phenylseleno ketones have been prepared by the reaction of enol acetates, ketone enolates or ketones with PhSeX, and have been utilized in a number of synthetic transformations.[2]

We wish to report a procedure for the regiospecific synthesis of α-phenylseleno ketones from monosubstituted alkenes. Reaction of 1 with PhSeBr[3] in DMSO gives 2; treatment of 2 with $AgPF_6$ in DMSO[4] followed by Et_3N affords 1-phenylseleno-2-alkanones (3) regiospecifically.



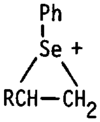
$$\underset{\underline{1}}{RCH{=}CH_2} \xrightarrow[DMSO]{PhSeBr} \underset{\underline{2}}{R\overset{Br}{\overset{|}{C}}HCH_2SePh} \xrightarrow[DMSO]{AgPF_6} \xrightarrow{Et_3N} \underset{\underline{3}}{R\overset{O}{\overset{\|}{C}}CH_2SePh}$$

a R = nBu
b R = nHex
c R = $PhCH_2$
d R = iPr



$$R\overset{\overset{+}{OSMe_2}}{\overset{|}{C}H}\text{-}CH_2SePh$$

4



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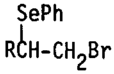
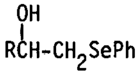


$$R\overset{SePh}{\overset{|}{C}H}\text{-}CH_2Br$$

6



$$R\overset{OH}{\overset{|}{C}H}\text{-}CH_2SePh$$

7

The conversion of 2 to 3 undoubtedly involves formation of an alkoxydimethylsulfonium salt 4. The possible intermediacy of the seleniranium ion 5 in the formation of 4 is suggested by the observations that 3a is also produced both when the pregenerated seleniranium ion 5a in toluene[5] is reacted with DMSO followed by Et_3N, and when the anti-Markownikoff adduct[3] 6a in toluene is added to a suspension of $AgPF_6$ in DMSO followed by addition of Et_3N; in both cases, no 2-phenylseleno hexanal was formed.

The α-phenylseleno ketones 3 were obtained in isolated overall yields of 65-75%. Also isolated were small amounts (10-20%) of the alcohols 7 despite rigorous attempts to maintain anhydrous conditions. Furthermore, reaction of E-3-hexene and E-6-dodecene under identical conditions led to the formation of 4-phenylseleno-3-hexanol and 7-phenylseleno-6-dodecanol, respectively, in greater than 60% isolated yield. The conversion of alkoxydimethylsulfonium salts to alcohols under anhydrous conditions has been observed previously.[6]

A typical experimental procedure follows:[7] a solution of 2a prepared from 1-hexene (1.0 mmol) and PhSeBr (1.0 mmol) in DMSO (1 mL) was added dropwise with stirring over 3 min to a suspension of $AgPF_6$ (1.2 mmol) in DMSO (1 mL) under an atmosphere of argon at 20 °C. The mixture was stirred for 2 min, dry Et_3N (4 mmol) was added dropwise, and stirring was continued for 30 min. The mixture was treated with ether, washed with water, dried ($MgSO_4$) and evaporated in vacuo. Purification by column chromatography on silica gel (10 g) with 10% ether-hexane, followed by evaporative distillation (125 °C, 0.02 mm) gave 3a (187 mg, 74%): ^1H NMR (CCl_4) δ 1.8-0.7 (m, 7H), 2.50 (t, J=7 Hz, 2H), 3.48 (s, 2H), 7.6-7.1 (m, 5H); IR (neat) ν 1715 cm^{-1}. Further elution of the column with 20% ether-hexane gave 7a (28 mg, 11%): ^1H NMR (CCl_4) δ 1.6-0.8 (m, 9H), 2.2 (bs, 1H), 2.75 (dd, J=12, 8Hz) and 3.08 (dd, J=12, 4 Hz) total 2H, 3.5 (m, 1H), 7.7-7.1 (m, 5H); IR (neat) ν 3450 cm^{-1}.

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4. Attempts to effect this conversion in the absence of Ag^+ were unsuccessful: a DMSO solution of 2a, with or without added base (Et_3N or pyridine) at temperatures from 25 °C to 150 °C failed to yield any 3a, but led only to decomposition. For silver-assisted dimethylsulfoxide oxidations of alkyl bromides, see B. Ganem and R. K. Boeckman, Jr., Tetrahedron Lett., 917 (1974).
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