Fragmentation of Selenoxides: a New Method for Dehydrogenation of Ketones

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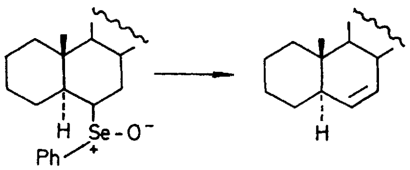
Summary The enol acetates of cyclohexanone and cyclopentanone react with PhSeBr and $AgOCOCF_3$ at low temperature to give, after work-up and oxidation ($NaIO_4$), cyclohex-2-en-1-one and cyclopent-2-en-1-one.

THE availability of simple methods for oxidising selenides quantitatively to the selenoxide level[1,2] and the reports that the selenoxides (**1**) and (**2**) collapse at, or below, room temp.[1,3] suggest that this fragmentation process, recently confirmed as a general phenomenon,[4] constitutes a gentle olefin synthesis. Its utility depends upon efficient methods becoming available for introducing selenium as, for example, PhSe into substrate molecules.†

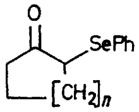
We have discovered mild conditions for using the electrophilic reagent, benzeneselenenyl bromide (PhSeBr),[5] to introduce the PhSe group. The process is illustrated by efficient dehydrogenation[6] of ketones. In the presence of silver trifluoroacetate (1·2 equiv.) the enol acetate of cyclohexanone reacts rapidly in ether solution at 0° to room temp. with benzeneselenenyl bromide (1·1 equiv.) to afford, after hydrolysis (aqueous tetrahydrofuran at room temp., *ca.* 0·02N in HCl), 2-phenylselenocyclohexanone (**3**; n = 2) in *ca.* 70% yield.‡ Oxidation of (**3**; n = 2) with NaIO$_4$ (3 mol) proceeds rapidly at room temp. in aqueous glyme and the derived selenoxide collapses smoothly ***in situ***,§ to give cyclohex-2-en-1-one [92% yield from (**3**; n = 2)]. Under similar conditions the enol acetate of cyclopentanone gives (**3**; n = 1) in *ca.* 62% yield¶ and oxidation affords cyclopent-2-en-1-one in 95% yield.§

The synthetic utility of benzeneselenenyl bromide has not previously been recognised;[7] the method reported here for converting ketones into αβ-unsaturated analogues involves high-yield stages and the unsaturated product is formed under very mild[6] conditions.[8]

(1)



(2)



(3)

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† Successful use (L. R. Williams and A. Ravve, *J. Amer. Chem. Soc.*, 1948, **70**, 3524, 1244) of benzyl chloromethyl selenide as a carbon alkylating agent is significant in this respect as it should offer a route to α-methylenelactones *via* the selenide oxidation–fragmentation process. For approaches to this important compound class see P. A. Grieco and K. Hiroi, *J.C.S. Chem. Comm.*, 1972, 1317.

‡ This compound has m.p. 56—57·5°, ν_{max} (CCl$_4$) 1710 cm^{-1}, δ (CCl$_4$) 3·75 (1H, t); molecular formula defined by mass measurement, and correct analysis.

§ Reaction mixture left overnight (yield of cyclohex-2-en-1-one after 2·5 h was 83%) and yield determined by g.l.c. relative to an internal standard. The ketone was isolated as its 2,4-dinitrophenylhydrazone.

¶Reaction run at −10° to +22° and hydrolysis done with aq. MeOH–NaHCO$_3$; oil ν_{max} (CCl$_4$) 1732 cm^{-1} δ (CCl$_4$) 3·62 (1H, t); molecular formula defined by mass measurement.

[1] R. Walter and J. Roy, *J. Org. Chem.*, 1971, **36**, 2561.

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[3] D. N. Jones, D. Mundy, and R. D. Whitehouse, *Chem. Comm.*, 1970, 86.

[4] K. B. Sharpless, M. W. Young, and R. F. Lauer, *Tetrahedron Letters*, 1973, 1979.

[5] O. Behaghel and H. Seibert, *Ber.*, 1932, **65**, 812; G. Bergson and S. Wold, *Arkiv Kerui*, **1963**, **19**, 215.

[6] *Cf.* A. G. Hortmann, D. S. Daniel, and J. E. Martinelli, *J. Org. Chem.*, 1973, **38**, 728; E. J. Corey and K. Osugi, *Pharm. Bull. Japan*, 1953, **1**, 99.

[7] For reaction of vinyl acetate in hot glacial acetic acid with methyl 2-nitrobenzeneselenenate see G. Hölzle and W. Jenny, *Helv. Chim. Acta*, 1958, **41**, 593.

[8] For use of other selenium reagents see K. B. Sharpless and R. F. Lauer, *J. Amer. Chem. Soc.*, 1973, **95**, 2697; D. L. J. Clive and C. V. Denyer, *J.C.S. Chem. Comm.*, 1973, 253.