# Fragmentation of Selenoxides: a New Method for Dehydrogenation of Ketones

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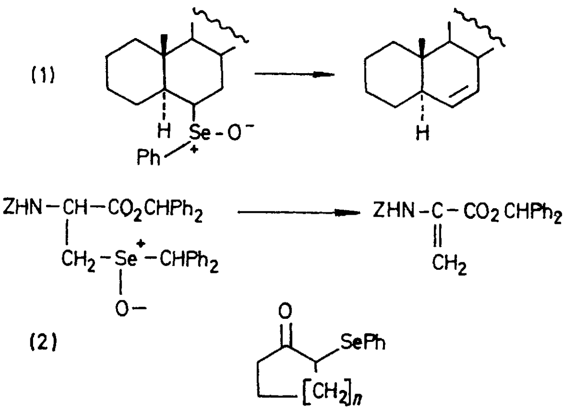
*Summary* The enol acetates of cyclohexanone and cyclopentanone react with PhSeBr and $AgOCOCF_3$ at low temperature to give, after work-up and oxidation ($NaIO_4$), cyclohex-2-en-1-one and cyclopent-2-en-1-one.

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]



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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°, $\nu_{max}$ ($CCl_4$) 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 $\nu_{max}$ ($CCl_4$) 1732 cm$^{-1}$ δ ($CCl_4$) 3·62 (1H, t); molecular formula defined by mass measurement.

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[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.