New Method for Preparing βγ-Unsaturated Ketones: Use of Phenylselenoacetaldehyde

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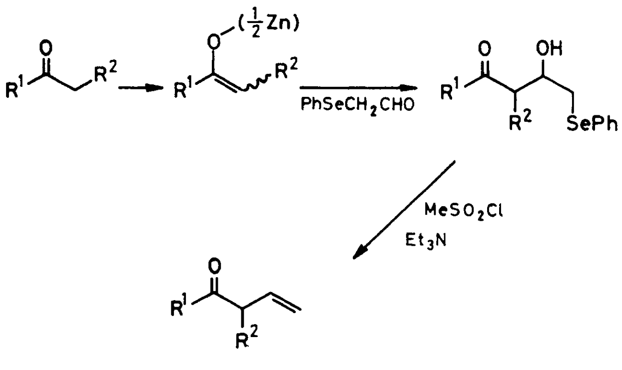
Summary Zinc enolates derived from ketones condense efficiently with phenylselenoacetaldehyde and the products are converted into *βγ*-unsaturated ketones by the action of methanesulphonyl chloride and triethylamine.

SYNTHETIC equivalents for vinyl carbonium ions may have important applications in the area, for example, of Cope[1] and oxy-Cope[2] rearrangements. However, such species are not well known.[3] We report that phenylselenoacetaldehyde[4] can be used in the sense of a vinyl carbonium ion equivalent to generate *βγ*-unsaturated ketones (Scheme).

A number of ketones (see Table) were converted into their zinc enolates[5]† which were treated with phenylselenoacetaldehyde to afford hydroxy-selenides. The latter were converted into the desired non-conjugated ketones by treatment with $MeSO_2Cl$ and Et_3N.[6] Although a number of procedures are known[7] for converting simple β-hydroxy-selenides into olefins, the one used here is the only generally satisfactory method of those that were tried. We also found that treatment of β-hydroxy-selenides with $COCl_2$ in the presence of pyridine (in ether solution at room temperature) and exposure of the derived chloroformate to NaI in MeCN (usually at reflux) also affords olefins but, of several cases (using the present series of β-hydroxy-δ-keto-selenides) in which we made a comparison, only (**6c**) and (**2c**) were formed efficiently by this route.



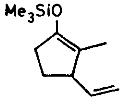
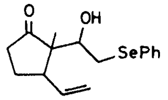
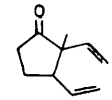
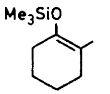
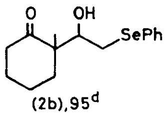
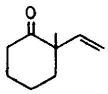
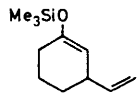
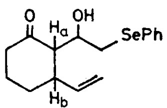
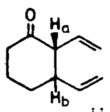
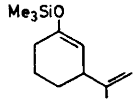
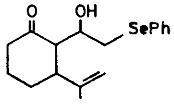
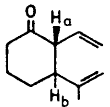
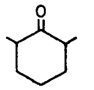
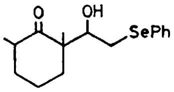
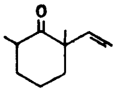
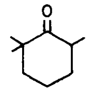
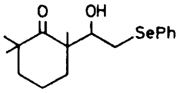
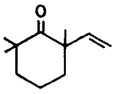
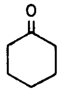
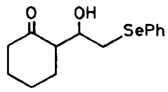
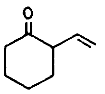
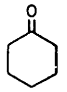
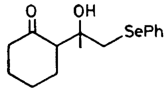
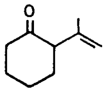
SCHEME

In a typical experiment, $ZnCl_2$ (1 equiv., as a saturated ethereal solution[5]) was added to an ethereal solution (*ca.* 0·4 M) of the lithium enolate at 0 °C. After 10 min, phenylselenoacetaldehyde (1 equiv.) in ether (*ca.* 0·8 M) was injected rapidly at 0 °C and after a further 5 min the mixture was quenched with aqueous NH_4Cl solution. The product could then be isolated with the results shown in the Table. For generating the double bond, the published procedure[6] was followed except that the reaction was run at room temperature and the $MeSO_2Cl$ was added very slowly (over *ca.* 1·5 h).‡

Phenylselenoacetaldehyde can be used in conjunction with 1,4-addition to enones [(**1a**) and (**4a**) being made[8] in this way] to provide compounds relevant to Claisen–Cope rearrangement chemistry.[1a] Alternatively, α-vinylation of a ketone followed by treatment with a vinyl *carbanion* provides access to substrates[2b] that can undergo ring expansion *via* oxy-Cope[2a] rearrangement, a recent example being[2b] the synthesis of acoragermacrone.

We generally worked with zinc enolates but the reaction of compound (**7a**) to give (**7b**) and (**7c**) illustrates the use of a boron enolate;[9] the initial lithium enolate (use of LDA) was quenched with Bu_2BCl and the resulting enol borinate was condensed[10] with phenylselenoacetaldehyde.§

TABLE

Starting material	Condensation product / %	Olefin / %
 (1a)	 (1b), 83	 (1c), 82[b]
 (2a)[c]	 (2b), 95[d]	 (2c), 82[e] 78[f]
 (3a)[g]	 (3b), 90[h]	 (3c), 92[i,j]
 (4a)[k]	 (4b), 89	 (4c), 80[i,l]
 (5a)	 (5b), 89	 (5c), 76
 (6a)	 (6b), 67	 (6c), 74 98[f]
 (7a)	 (7b), 78	 (7c), 54
 (7a)	 (8b), 67	 (8c), 62 (91[m])

[a] Yields refer to isolated material except for (**5c**), (**7c**), and (**8c**), which were determined by n.m.r. spectroscopy using an internal standard. The condensation products are diastereoisomeric mixtures. Where these were separable, the *individual* components were characterized. [b] Probably a single isomer (n.m.r., 200 MHz). [c] G. Stork and P. F. Hudrlick, *J. Am. Chem. Soc.*, 1968, **90**, 4464. [d] Major diastereoisomer has m.p. 78—80 °C. [e] E. N. Marvell and R. Rusay, *J. Org. Chem.*, 1977, **42**, 3336. [f] $COCl_2$–NaI method. Yield determined by n.m.r. spectroscopy. [g] Neither satisfactory Si nor O analyses were obtained. Correct mass measurement. [h] Only two diastereoisomers are formed (in a ratio of *ca.* 60 : 40). Both have *trans* substituents: J_{ab} 10 and 8 Hz for the major and minor isomers, respectively. Minor isomer has m.p. 46·5—47 °C. [i] The major diastereoisomer of the precursor was used. [j] J_{ab} 10 Hz. [k] Made by the method of ref. 8. See also H. O. House, R. A. Latham, and C. D. Slater, *J. Org. Chem.*, 1966, **31**, 2667. [l] J_{ab} 11 Hz. [m] 91% after correction for recovered starting material. The olefin is a known compound: A. G. Gasanov, S. D. Mekhtiev, and M. R. Musaev, *Azerb. Khim. Zh.*, 1975, (3), 6: *Chem. Abstr.*, 1976, **84**, 58704 h.

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† For reactions of (**1a**)—(**4a**) the Li enolate, generated from the silyl enol ether by the action of MeLi, was treated with $ZnCl_2$. For reactions of (**5a**), (**6a**), and (**7a**) to give (**5b**), (**6b**), and (**8b**) [but not (**7b**)], respectively, the ketone itself was treated with lithium di-isopropylamide (LDA), and then with $ZnCl_2$.

‡ For experiments using *ca.* 0·7 mmol of hydroxy-selenide.

§ In this case work-up involved addition of $Me_3N^+–O^-$ to remove boron species and to liberate (**7b**) (reference 11).

The reaction of (**7a**) to give (**8b**) and (**8c**) establishes that α-isopropenylation of a ketone is also possible by using phenylselenoacetone.[12]

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