Photochemical Reduction of Carbon–Carbon and Carbon–Nitrogen Double Bonds by Benzeneselenol

By M. John Perkins,* Brian V. Smith, and Eric S. Turner
(*Department of Chemistry, Chelsea College, Manresa Road, London* SW3 6LX)

Summary Irradiation of β-aryl-$\alpha\beta$-unsaturated carbonyl compounds and of some imino-derivatives of benzaldehyde in the presence of benzeneselenol leads to formation of the corresponding saturated compounds.

Compounds containing selenium have received much recent attention as reducing agents. Benzeneselenol has been used to reduce sulphoxides,[1,2] disulphides,[1] diazonium salts,[3] and aromatic azo-compounds.[1] A recent report[4] on the reduction of various nitro-, nitroso-, and hydroxylamino-arenes is in accord with our own observations.[5] We have now examined the possibility of reduction of other functional groups with benzeneselenol and here outline some preliminary findings. The principal results are summarised in the Table.

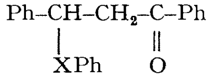
Table

Entry	Starting material	Reagents and Conditions [a,b]	Product	Comment [c,d]
1	*trans*-Cinnamaldehyde	i	3-Phenylpropanal	Rapid
2	,, ,,	ii	,,	Very slow
3	Chalcone	i	1,3-Diphenylpropan-1-one	Rapid
4	Cinnamic acid	i	3-Phenylpropionic acid	Slow
5	Ethyl cinnamate	i	—	No reaction [e]
6	(**1**)	i	1,3-Diphenylpropan-1-one	Rapid
7	(**1**)	iii	,,	Rapid
8	(**2**)	i	,,	Very slow
9	(**2**)	iii	—	No reaction
10	Benzyl phenyl selenide	i	Toluene	Rapid
11	α-Methylstyrene	i	1-Phenylseleno-2-phenylpropane	[f]
12	*trans*-Stilbene	i	1,2-Diphenylethane	Slow [g]
13	(**3**; R = H)	i	(**4**; R = H)	95%
14	(**3**; R = Me)	i	(**4**; R = Me)	95%
15	(**3**; R = Me)	i [b]	(**4**; R = Me)	90%
			Benzylamine	10%
			N-Methylaniline	10%
16	Benzaldehyde oxime	i	*N*-Benzylhydroxylamine	70%
17	Benzylideneaniline	i	*N*-Benzylaniline	60%

[a] i, PhSeH/$h\nu$, ii PhSeH/dark/reflux, iii, PhSH/$h\nu$. All reactions were carried out in $CDCl_3$ or CD_3OD (for reactions monitored by ^1H n.m.r. spectroscopy) or EtOH under N_2 and irradiation with a 300 W sunlamp (except entry 2). [b] With the exception of entry 15 (5 equiv.), the reductions were carried out using an excess (3 equiv.) of benzeneselenol or benzenethiol. [c] Rapid reductions were substantially complete (>95% consumption of starting material) in less than 2 h and resulted in essentially quantitative reduction to the products given. [d] Yields quoted are for reactions carried out in n.m.r. tubes and were determined by addition of an internal integration standard. Isolated yields were considerably lower. [e] No adduct formation. [f] The adduct did not undergo further reduction. [g] Quantitative formation of product.

It is known that benzeneselenol readily forms 1,2-adducts with many $\alpha\beta$-unsaturated carbonyl compounds The use of an excess of benzeneselenol in the preparation of adducts of maleic and fumaric acids has been shown[6] to give rise to succinic acid Benzeneselenol has also been implicated[7] in the reduction of cinnamic acid with a mixture of tetralin and diphenyl diselenide

We find that the reductions of chalcone and cinnamaldehyde by benzeneselenol in refluxing ethanol or chloroform, which are slow in the dark, are greatly accelerated on irradiation (sunlamp) The selenol adduct (**1**) of chalcone is rapidly reduced by both benzeneselenol and benzenethiol on irradiation, whilst the thiol adduct (**2**) shows little such tendency Cinnamic acid is only slowly reduced under our conditions, possibly owing to an unfavourable equilibrium in the formation of the adduct More surprisingly, ethyl cinnamate is inert under similar conditons



$$\underset{\textstyle XPh}{Ph\text{–}\underset{|}{C}H}\text{–}CH_2\text{–}\underset{\textstyle O}{\underset{\|}{C}}\text{–}Ph$$

(**1**) X = Se
(**2**) X = S

Imino-derivatives of benzaldehyde are not reduced by benzeneselenol in the dark, even at 80 °C On irradiation, however, rapid reduction takes place Monitoring of the reaction (by ^{1}H n m r spectroscopy) indicates that the reductions have the stoicheiometry shown in equation (1)

$$\underset{(\mathbf{3};\ R = H\ \text{or}\ Me)}{PhCH{=}N\text{–}NRPh} + 2PhSeH \rightarrow \underset{(\mathbf{4})}{PhCH_2NH\text{–}NRPh} + PhSe\text{–}SePh \quad (1)$$

The reduction of benzaldehyde *N*-methyl-*N*-phenylhydrazone (**3**, R = Me) (entry 14 in the Table) indicates that such reductions need not take place *via* the azo tautomers

The efficiency of reduction of (**3**, R = Me) by benzeneselenol proved to be comparable to that of the photochemical reduction of benzophenone by propan-2-ol when the reactions were carried out concurrently under near-identical conditions This qualitative observation would appear to be inconsistent with a radical chain process for the benzeneselenol reduction of hydrazones Derivatives of aliphatic ketones are apparently not reduced under similar conditions

Ketones and aldehydes have recently been shown[8] to react with methaneselenol and zinc chloride to give either the selenoketal (**5**) or the selenide (**6**) (according to the quantity of zinc chloride used), probably in a stepwise fashion We find that in analogues of (**6**) in which R = Ph, such as benzyl phenyl selenide or the adduct (**1**), the additional stabilisation (of the incipient radical ?) is sufficient to allow further photochemical reduction by benzeneselenol to give the hydrocarbon (see entries 6 and 10 in the Table)

$$R\text{–}C(\ O)\text{–}R' \xrightarrow{1} \underset{(\mathbf{5})}{R\text{–}C(SeMe)_2\text{–}R'} \xrightarrow{1} \underset{(\mathbf{6})}{R\text{–}C(SeMe)(H)\text{–}R'}$$

i, $MeSeH\text{–}ZnCl_2$

The implication is that the photochemical reductions of benzylic selenides depend either on S_H2 displacements of benzylic radicals from selenium by PhSe (or PhS , entry 7), or on direct photolysis of the benzyl–Se bond This latter possibility has analogies in the photoextrusion of sulphur from dibenzyl sulphides,[9] as well as in the photolysis of dibenzyl diselenide[10] which yields dibenzyl selenide *via* scission of a C–Se bond The identities of the initiation and termination steps responsible for the smooth reactions which are observed are, however, unclear

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