Novel Functional Group Transformations involving Alkyl Phenyl Selenones

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Alkyl phenyl selenones readily undergo substitution reactions, and are valuable precursors of epoxides on reaction with aldehydes in the presence of bases.

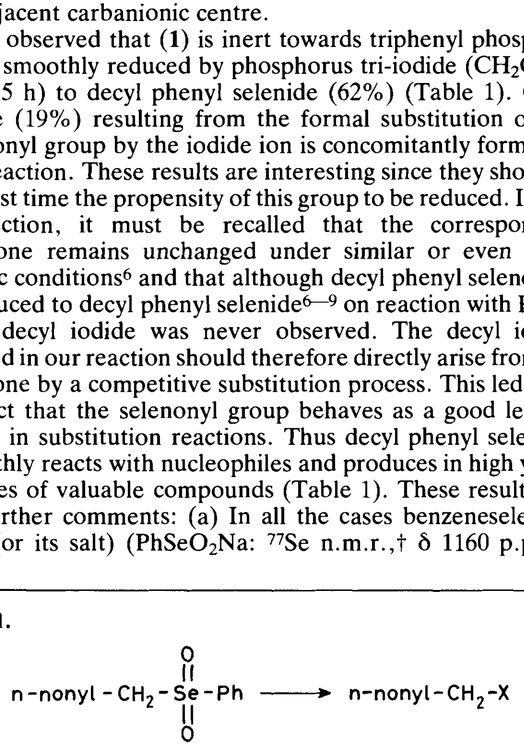
While the reactivity of sulphones is well documented,[1] little is known about their selenium analogues, namely the selenones.[2—5] We now report preliminary results concerning the exceptional reactivity of this quite unexplored functional group. We decided to take decyl phenyl selenone (**1**) as a model and to look at the aptitude of the phenyl selenonyl moiety to be reduced, to act as a leaving group, and to stabilize an adjacent carbanionic centre.

We observed that (**1**) is inert towards triphenyl phosphine but is smoothly reduced by phosphorus tri-iodide (CH_2Cl_2, 0 °C, 0.5 h) to decyl phenyl selenide (62%) (Table 1). Octyl iodide (19%) resulting from the formal substitution of the selenonyl group by the iodide ion is concomitantly formed in this reaction. These results are interesting since they show for the first time the propensity of this group to be reduced. In this connection, it must be recalled that the corresponding sulphone remains unchanged under similar or even more drastic conditions[6] and that although decyl phenyl selenoxide is reduced to decyl phenyl selenide[6—9] on reaction with PI_3 or P_2I_4, decyl iodide was never observed. The decyl iodide formed in our reaction should therefore directly arise from the selenone by a competitive substitution process. This led us to suspect that the selenonyl group behaves as a good leaving group in substitution reactions. Thus decyl phenyl selenone smoothly reacts with nucleophiles and produces in high yields a series of valuable compounds (Table 1). These results call for further comments: (a) In all the cases benzeneseleninic acid (or its salt) ($PhSeO_2Na$: ^{77}Se n.m.r.,† δ 1160 p.p.m., H_2O) is concomitantly formed. This compound can be easily removed from the organic layer by washing with aqueous sodium bicarbonate solution. (b) In several instances (Table 1), decyl alcohol is also formed simultaneously in 5—10% and in some cases up to 20% yield. It is unclear if it arises by direct substitution of the selenonyl group by some water adventitiously present in the medium or if selenone–seleninate rearrangement takes place instead. (c) Decyl alcohol (85% yield) can be directly prepared from decyl phenyl selenide on reaction with *m*-chloroperbenzoic acid and potassium hydroxide in THF (*m*-CPBA: 5 mol equiv., KOH: 6.6 mol equiv., reflux, 24 h). The corresponding methyl ether (57% yield) can also be prepared in a similar way from the selenide and *m*-CPBA in MeOH (*m*-CPBA: 5 mol equiv., 20 °C, 2.5 h). It must be recalled that in the former reaction recently described by Uemura[10] it was suggested that decyl methyl ether was formed by nucleophilic displacement of the selenonyl group on the selenone transiently formed. We were rather surprised to find that methanol (used as the solvent) alone or mixed with one equivalent of *m*-chlorobenzoic acid does not react at 20 °C to a reasonable exent with decyl phenyl selenone. However methyl decyl ether is obtained in good yield (87%) if *m*-CPBA is added to the methanolic solution of the selenone. These results suggest that many substitution reactions could be conveniently and directly performed on the selenide when carried out in the presence of an oxidant.

We have also looked at the reactivity of decyl selenone towards some organometallic derivatives. n-Butyl-lithium leads to a mixture of compounds whose structures have not yet been investigated. On the other hand, Grignard reagents react under very mild conditions (Et_2O, 0.1 h) with this selenone and unexpectedly produce decyl halides in high yields. Thus decyl bromide and chloride were obtained in 77 and 51% yield respectively, on reaction with EtMgBr (or Pr^iMgBr) or with Bu^nMgCl (Table 1). As expected $KOBu^t$ in THF acts as a base rather than as a nucleophile towards decyl phenyl selenone and interestingly 1,2-epoxy-1-phenylundecane is formed in high yield if benzaldehyde is present in the reaction medium (Scheme 1).

These results show that selenones possess reactivity which is quite different from the one already described for the analogous sulphones. This is mainly due to the aptitude of the selenonyl group to act as a good leaving group. Competition experiments in ethanolic solution show that the phenyl selenonyl group is a better leaving group than bromide and even iodide ions. Indeed when sodium thiophenolate (1 equiv.) is treated (EtOH, 20 °C) with an excess of decyl phenyl selenone (5 equiv.) and nonyl halides (bromide or iodide, 5

Table 1.

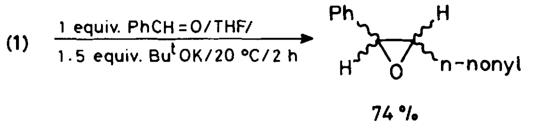


$$\text{n-nonyl-CH}_2\text{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{\text{Se}}}\text{-Ph} \longrightarrow \text{n-nonyl-CH}_2\text{-X}$$

(**1**)

Number of mol. equiv. of reagent	Conditions[a]	X	% Yield
1.1 PI_3	$CHCl_3$, 0 °C, 0.5 h	SePh	62
		I	19
2 NaI	acetone, 20 °C, 1 h	I	97
1.5 $MgBr_2$	Et_2O, 0 °C, 0.5 h	Br	81
5 NaN_3	DME–H_2O, 20 °C, 0.7 h	N_3	93
2 KCN	DME–H_2O, 75 °C, 2 h	CN	66
		OH	19
1.5 KOH	THF, 80 °C, 22 h	OH	76
H_2O	DMF, 80 °C, 1.25 h	OH	95
1.1 MeONa	MeOH, 20 °C, 3 h	OMe	73
1.1 PhSNa	EtOH, 20 °C, 0.5 h	SPh	94
1.5 EtMgBr	Et_2O, 0 °C, 1 h	Br	77
1.5 Pr^iMgBr	Et_2O, 0 °C, 1 h	Br	76
1.5 Bu^nMgCl	Et_2O, 0 °C, 1 h	Cl	51

[a] DME = dimethoxyethane, THF = tetrahydrofuran, DMF = dimethyl formamide.



Scheme 1

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† Dimethyl selenide was used as external reference.

equiv.), decyl phenyl sulphide is isolated as the sole reaction product (|g.c.|[2] *i.e.* chromatography with capillary columns). These results should however be confirmed in other solvents and using other nucleophiles.

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