Rearrangement of Aryl Alkyl Selenoxides to Aldehydes

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Summary On heating, *meta*- and *para*-substituted benzyl phenyl selenoxides rearranged and decomposed to yield benzaldehydes and diphenyl diselenide in high yield.

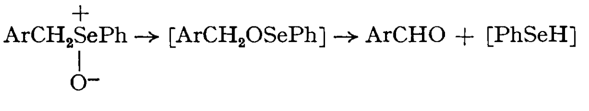
REARRANGEMENT of benzyl methyl sulphoxides to give aldehydes has been reported.[1] This reaction, formally analogous to the Meisenheimer rearrangement of tertiary amine oxides to substituted hydroxylamines,[2] only takes place in substrates in which β-elimination to olefin is prevented by the absence of hydrogen on the carbon atom β to the sulphoxide group. Also, unlike the easy β-elimination of sulphoxides to give olefins, high temperatures (210—280 °C) are required to convert benzyl methyl sulphoxides into benzaldehydes. In many ways, selenium compounds react similarly to their sulphur analogues but reaction is frequently much easier.[4] Thus, β-elimination of selenoxides to give olefins proceeds readily at room temperature[5] and, whereas epoxides and episulphides are well known, episelenides have never been isolated.[6] Because of this reduced stability of selenium compounds, we have examined the effect of heat on selenoxides, $ArCH_2Se(:O)Ph$, as a possible synthetic route to aromatic aldehydes.

TABLE. Yield of substituted benzaldehyde from substituted benzyl phenyl selenoxide, $ArCH_2Se(:O)Ph$[a].

Ar (% yield):[b] Ph (78), p-MeC_6H_4 (61), m-MeC_6H_4 (76), o-MeC_6H_4 (*ca.* 10), p-$NO_2C_6H_4$ (71), m-$NO_2C_6H_4$(40), p-ClC_6H_4 (76), p-$MeOC_6H_4$ (83)

[a] All the selenoxides gave satisfactory elemental analyses and n.m.r. spectra. [b] Yield based on isolation as 2,4-dinitrophenylhydrazone.

Treatment of a benzyl halide, $ArCH_2X$, with phenylselenide anion, prepared by reduction of diphenyl diselenide with sodium borohydride,[7] afforded the selenide, $ArCH_2SePh$, as a low-melting solid. The corresponding selenoxide was prepared quantitatively by oxidation with sodium metaperiodate in dioxan–water at 0 °C. On heating the selenoxide alone or in solution (xylene) to 110—130 °C for 2—3 min, benzaldehydes were formed [reaction (1)] in good yield (Table). The aldehydes were identified and estimated as 2,4-dinitrophenylhydrazones. The only other major



$$ArCH_2\overset{+}{Se}(\text{O}^-)Ph \rightarrow [ArCH_2OSePh] \rightarrow ArCHO + [PhSeH] \quad (1)$$

product of reaction was diphenyl diselenide which is assumed to have been formed by the ready aerial oxidation of phenylselenol [reaction (1)]. The mechanism of the reaction is under investigation but preliminary experiments suggest the presence of radical intermediates.

Attempted oxidation of *o*-methylbenzyl phenyl selenide with a variety of reagents gave mainly phenylseleninic acid and no selenoxide could be isolated, possibly owing to the low stability and steric difficulty of formation of the Se–O bond;[8] small quantities of *o*-methylbenzaldehyde were isolated directly from these oxidations carried out at room temperature.

(*Received*, 30*th October* 1975; *Com.* 1220.)

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