Base Treatment of Benzylic Selenonium Salts. [2,3] Sigmatropic Rearrangements *vs*. Nucleophilic Displacement

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Summary Treatment of certain benzylic selenonium salts with a variety of bases resulted in nucleophilic attack to yield either an alkylation or a benzylation of the base, while the use of sodium amide in liquid ammonia as base generated a selenonium ylide which gave *ortho* substitution of the benzyl group *via* [2,3]sigmatropic rearrangement

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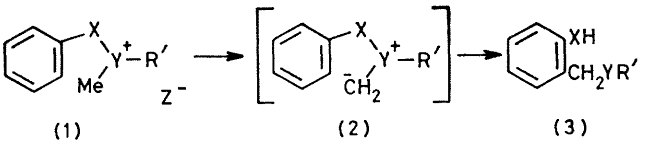
THE [2,3] sigmatropic rearrangement of ylides derived from base treatment of aryl substituted derivatives of onium salts has been widely used as a selective method for the *ortho* substitution of aromatic substrates[1–4] Onium salts of general formula (**1**) can usually be converted into (**2**) with a wide variety of bases under a range of conditions

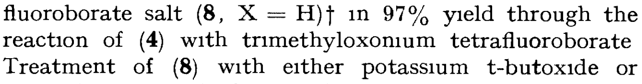


(1) (2) (3)

(**a**) X = CH_2, Y = NR (ref 1)
(**b**) X = CH_2, Y = S (ref 2)
(**c**) X = O, Y = S (ref 3)
(**d**) X = NH, Y = S (ref 4)

In most instances (**2**) spontaneously undergoes a [2,3]-sigmatropic rearrangement which results in substitution of the *ortho* position and the eventual formation of (**3**) We now report what we believe to be the first examples of the rearrangement of selenonium ylides of formula (**2**, X = CH_2, Y = Se)[5]

Treatment of benzyl phenyl selenide[6] with methyl iodide gave an equilibrium mixture of (**4**), (**5**), (**6**), and (**7**) On treatment of this mixture with potassium t-butoxide, we

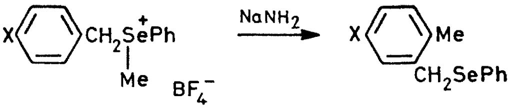


$$\mathrm{PhSeCH_2Ph} + \mathrm{MeI} \rightleftharpoons \mathrm{Ph}\underset{\substack{|\\ \mathrm{Me\ I^-}}}{\overset{+}{\mathrm{Se}}}\mathrm{CH_2Ph} \rightleftharpoons \mathrm{PhSeMe} + \mathrm{PhCH_2I}$$

(**4**) (**5**) (**6**) (**7**)

found no evidence for the generation of an ylide from (**5**) Instead, we obtained a mixture of (**4**), (**6**), methyl t-butyl ether, and benzyl t-butyl ether Since it was unclear as to whether the ethers had resulted from nucleophilic attack on (**5**) or on the respective iodides, we prepared the tetrafluoroborate salt (**8**, X = H)[†] in 97% yield through the reaction of (**4**) with trimethyloxonium tetrafluoroborate Treatment of (**8**) with either potassium t-butoxide or triethylamine resulted in the formation of approximately a 9:1 mixture of (**6**) and (**4**), illustrating the tendency of the selenide to act as a leaving group

The desired [2,3]sigmatropic rearrangement was achieved through the use of sodium amide in liquid ammonia Addition of (**8**, X=H) to 1 1 equiv of sodium amide in liquid ammonia at −78 °C (1·5 h), followed by warming to 25 °C, gave 16% of (**9**, X=H) In addition, 26% of (**6**) and trace amounts of *trans*-stilbene were formed.[7]



(8) (9)

[†] Satisfactory elemental analysis and/or exact mass molecular weights were obtained on all new compounds

With 2·0 equiv. of sodium amide we obtained 17% of (**9**; X=H), 19% of (**6**), and 11% of *trans*-stilbene. In a similar manner, treatment of (**8**; X=Cl) with 2·0 equiv. of sodium amide gave 37% of (**9**; X=Cl), 16% of (**6**), and 6% of *p,p'*-dichloro-*trans*-stilbene.

Treatment of benzyl methyl selenide with methyl fluorosulphonate gave 88% of the fluorosulphonate salt, which on treatment with 1·2 equiv. of sodium amide in liquid ammonia at −78 °C yielded 43% of 2-methylbenzyl methyl selenide. Similar treatment of 4-chlorobenzyl methyl selenide with methyl fluorosulphonate gave a 98% yield of the corresponding selenonium fluorosulphonate salt, which yielded 50% of 5-chloro-2-methylbenzyl methyl selenide after a [2,3]sigmatropic rearrangement under our conditions.

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[5] The [2,3] sigmatropic rearrangement of a selenium substituted sulphonium salt has been reported to occur in 2% yield (M. R. Detty, *J. Org. Chem.*, 1979, **44**, 4528).

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[7] Ample precedent exists for the formation of *trans*-stilbene from onium (sulphonium) salts under basic conditions (C. G. Swain and E. R. Thornton, *J. Am. Chem. Soc.*, 1961, **83**, 4033).