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

By Paul G Gassman,* Takashi Miura, and Allen Mossman

(Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455)

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

THE [2,3] signatropic rearrangement of vlides 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)
(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 selenide⁶ with methyl iodide gave an equilibrium mixture of (4), (5), (6), and (7) On treatment of this mixture with potassium t-butoxide, we

$$PhSeCH_{2}Ph + MeI \rightleftharpoons PhSeCH_{2}Ph \rightleftharpoons PhSeMe + PhCH_{2}I$$

$$|$$

$$Me I^{-}$$
(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 11 equiv of sodium amide in liquid ammonia at -78 °C ($1\cdot5$ 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



† 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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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).