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RADICAL C-Se BOND CLEAVAGE OF SELENONIUM SALTS WITH GRIGNARD REAGENTS OR MAGNESIUM METAL

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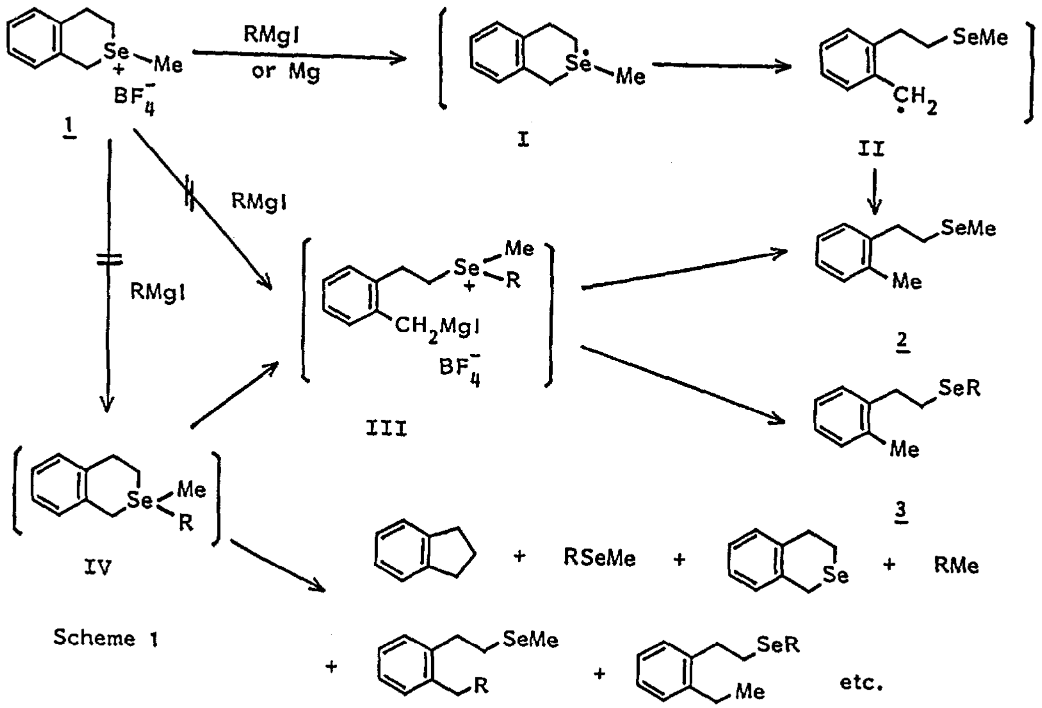
Abstract: The reaction of 2-methylisoselenochromanium salt with Grignard reagents afforded the reductive ring-opened product by the single electron transfer (SET) mechanism, not by the self-decomposition of σ-selenurane. The same reduction was observed in the reaction of the selenonium salt with magnesium metal. Some other selenonium salts were easily reduced by magnesium metal to give ring-opened products.

Selenonium salts react with alkyl- or aryl-lithiums to form unstable σ-selenuranes[1] and/or to exchange their substituents (ligands) on the selenium atom.[2] In contrast, we have just found a new reaction in which the C-Se bond of cyclic selenonium salts was homolytically cleaved by Grignard reagents. In this communication, we describe the reactions of 2-methylisoselenochromanium salt with some Grignard reagents and of some cyclic selenonium salts with magnesium metal.

2-Methylisoselenochromanium tetrafluoroborate (1) reacted with 3 molar equivalents of ethylmagnesium iodide at 0°C to give a ring-opened product, 2-(2-methylselenoethyl)toluene (2)[3] in 73% yield (Scheme 1). The reaction of 1 with phenylmagnesium iodide similarly afforded 2 in quantitative yield. Surprisingly, 2 was not obtained in the reaction of 1 with phenylmagnesium bromide. These results suggest that the nucleophilic attack of Grignard reagents on the selenium atom does not occur. If Grignard reagents attack on the selenium atom to form the intermediate (III) followed by decomposition to product 2, the reaction of 1 with phenylmagnesium iodide would have to give 2-(2-phenylselenoethyl)toluene (3) (R = Ph). But 3 was not obtained. On the other hand, if the Grignard reagents form the σ-selenuranes (IV) whose decomposition gives 2, some ligand-coupled products can be expected to form. But they were not obtained.

The different reactivity between phenylmagnesium iodide and bromide would be explained by the assumption that the former donates an electron to a selenonium salt more easily than the latter. In the case of the reaction of 1 with allylmagnesium bromide, a fairly good single electron transfer

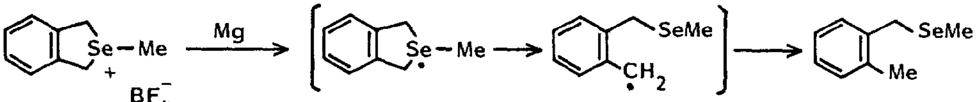


Scheme 1

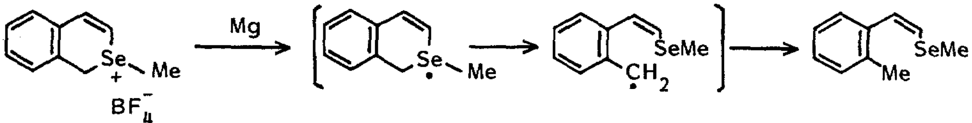
(SET) reagent[4], 2 was obtained in 50% yield. On the other hand, 1 similarly reacted with magnesium metal to give 2 in 82% yield.

These results show that the Grignard reagents or magnesium metal give a single electron to the selenium atom of 1 to form a radical (I). The easy C-Se bond cleavage of the unstable intermediate (I) forms a benzyl radical (II), which abstracts the hydrogen from the solvent to give 2.

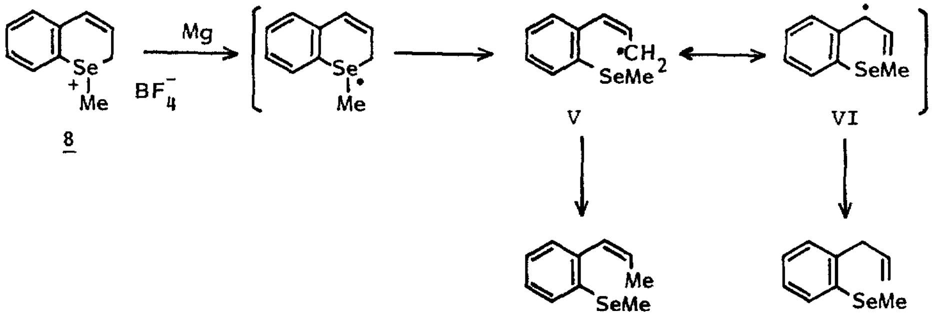
We applied this new reaction to some other selenonium salts.[5] A typical experiment is shown as follows. Magnesium (3 mmol) was added to the suspension of selenonium salt (1 mmol) in dry THF (20 ml) and the mixture was stirred for 30 h at room temperature. Saturated aqueous ammonium chloride solution was added to the mixture. The mixture was extracted with ether. The ether layer was washed with water, dried over magnesium sulfate, and evaporated under reduced pressure. The residue was separated by preparative TLC on silica gel. Five-membered cyclic selenonium salt 4 or vinyl selenonium salt 6 similarly reacted to give a ring-opened product 5 or 7, respectively (eq. 1,2). In the case of allyl selenonium salt 8, styrene 9 and allylbenzene derivative 10 were obtained in 44% and 26% yields, respectively (eq. 3). This reaction indicates that the allyl radical (V) isomerizes to the radical (VI). β-Ketoselenonium salt 11 generated predominantly α-carbonylmethyl radical (VII) rather than the benzyl radical



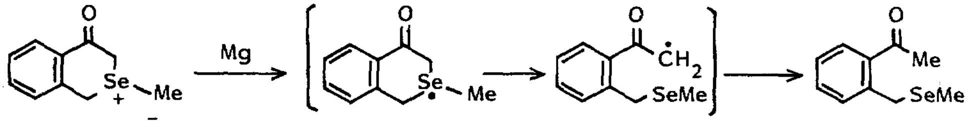
4 5 64% (eq. 1)



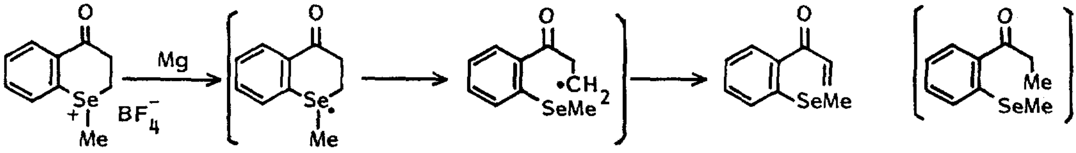
6 7 65% (eq. 2)



8 9 44% 10 26% (eq. 3)

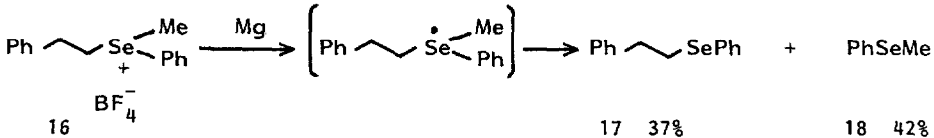


11 VII 12 86% (eq. 4)

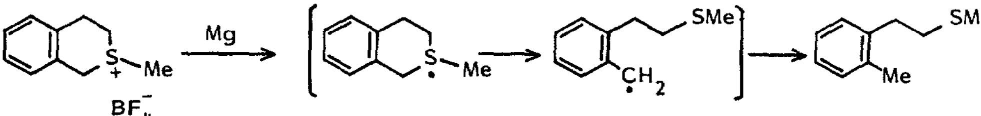


13 VIII 14 50% 15

(eq. 5)



16 17 37% 18 42% (eq. 6)



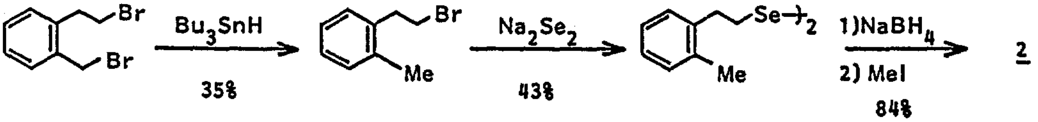
19 20 70% (eq. 7)

and gave the acetophenone derivative 12 (eq. 4), while γ-ketoselenonium salt 13 afforded the enone derivative 14 (eq. 5). Enone 14 would be formed by dehydrogenation of a β-carbonylethyl radical (VIII) by the other radicals because ethyl 2-methylselenophenyl ketone (15), one of the disproportional reaction products of the radical (VIII) was not isolated. This SET reduction proceeded even in the cases of acyclic selenonium salt 16 and sulfonium salt 19 (eq. 6,7). From a different point of view, the sulfur radicals having nine electrons have been recently proposed as one of the resonance hybrids of $RSCO\text{-}CH_2CH_2\cdot$ and $RS\text{-}CH_2CH_2\cdot$.[6]

Application of this easy cleavage of C-Se or C-S bond of the onium salts to some organic syntheses is now going on.

References

1. G. Wittig and H. Fritz, Ann. Chem., 1952, 577, 39; W. Dumont, P. Bayet, and A. Krief, Angew. Chem. Int. Ed., 1974, 13, 804.
2. M. Hori, T. Kataoka, H. Shimizu, C. F. Hsu, Y. Asahi, and E. Mizuta, Chem. Pharm. Bull., 1974, 22, 32.
3. The structure of 2 was determined by comparison with an authentic sample synthesized as shown below.



4. 'Comprehensive Organometallic Chemistry' Vol. 1, p. 155, ed. by G. Wilkinson, Pergamon Press, New York, 1982.
5. Satisfactory analytical and spectral results were obtained for all new compounds described in this paper.
6. M. Tada, T. Nakamura, and M. Matsumoto, J. Am. Chem. Soc., 1988, 110, 4647; M. Tada and S. Tomoki, Chem. Ind. (London), 1986, 790; J. E. Baldwin, R. M. Adlington, T. W. Kang, E. Lee, and C. J. Schofield, J. Chem. Soc., Chem. Comm., 1987, 104.

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