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NOVEL REDUCTION OF CHLORINE ADDUCTS OF ARYL AND ALKYL SELENIDES WITH DIMETHYL SULFOXIDE

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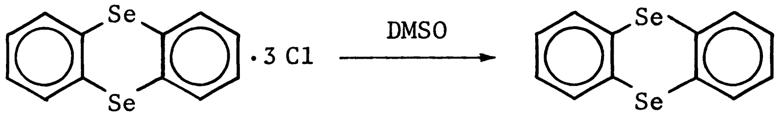
The adducts of chlorine with diaryl selenides such as selenanthrene, diphenyl selenide, and selenoxanthone have been found to be reduced to the corresponding selenides in dimethyl sulfoxide forming chloromethyl methyl sulfoxide and hydrogen chloride. Similarly, dimethyl selenide dichloride was reduced to dimethyl selenide in the presence of a base.

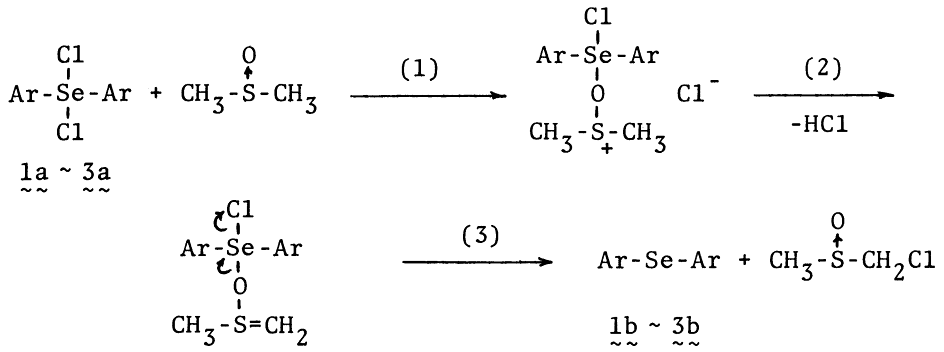
In the course of a structural study of selenanthrene trichloride (1a) by means of NMR spectroscopy, the compound was found to be reduced to the parent selenanthrene (1b) when dissolved in dimethyl sulfoxide (DMSO). The reaction proved to be applicable to other aryl and alkyl selenide dichlorides. Since the reductive properties of DMSO are less known,[1)] we wish to report the reactions briefly.



1a 1b

The reaction of 1b with chlorine in methylene dichloride gave pale yellow precipitates which consisted of 1b and chlorine atom in a 1 : 3 ratio by elemental analyses.[2)] The adduct 1a did not dissolve in usual solvents, e.g., chloroform, dichloromethane, methanol, THF and dioxane. When 1a was dissolved in DMSO-d_6 to measure ^{1}H and ^{13}C NMR spectra, the obtained spectra were not those expected for 1a but those of parent selenide 1b. Additional signals due to chloromethyl methyl sulfoxide were observed. The resulting reaction mixture was acidic. These results show that 1a was reduced to 1b with the formation of chloromethyl methyl sulfoxide and hydrogen chloride.[3)] Diphenyl selenide dichloride (2a) and selenoxanthone dichloride (3a) were also reduced to corresponding selenides 2b and 3b, respectively. When dimethyl selenide dichloride (4a) and selenoanisole dichloride (5a) were dissolved in DMSO-d_6, the signals due to 4a and 5a disappeared gradually but those of dimethyl selenide (4b) and selenoanisole (5b) were not found in the NMR spectra. The reactions of 4a and 5a were complex and eventually some metallic selenium precipitated out of the solution.

There are two mechanisms conceivable for the reaction. One assumes slight dissociation of the adduct into the selenide and molecular chlorine. The latter can react with solvent DMSO to give chloromethyl methyl sulfoxide and hydrogen chloride. The other is a Pummerer reaction-type mechanism which consists of three steps: (1) the ligand exchange of a chlorine atom with DMSO, (2) deprotonation from the methyl group, and (3) elimination reaction to give the products. Since the dissociation of chlorine is considered to be a very unfavorable process in the selenide adducts,[4] and the chlorination of DMSO with molecular chlorine gives a complicated mixture of products,[5] we are inclined to adopt the second mechanism.



Whereas the reduction of diaryl selenide chlorides proceeded almost quantitatively, that of methyl selenide dichlorides was not successful. However, the formation of a small amount of **4b** was confirmed from its characteristic smell in the reaction mixture. The methyl carbons of **4b** had the NMR signal at δ 6.3 in DMSO-d_6. When excess hydrogen chloride was introduced in the solution, the signal moved downfield to δ 44.1 showing the formation of protonated selenide $CH_3Se^+HCH_3Cl^-$. This peak disappeared in a few minutes. Thus it is highly likely that the methyl selenides once formed in the reaction may have decomposed under the acidic reaction conditions. Dimethyl selenide was obtained in ca. 50 % yield when the reaction of dimethyl selenide dichloride in DMSO was carried out in the presence of excess sodium bicarbonate. When excess sodium carbonate was used, dimethyl selenoxide was produced in ca. 90 % yield in addition to ca. 10 % of **4b**.

References

1) S. Oae, "Organic Chemistry of Sulfur", Plenum: New York, Chapt. 8, 1977.
2) The details will be described elsewhere.
3) There is a precedent of a more easily dissociated bromine adduct. The mixed bromine adduct of phenoxyselenine and phenoxytellurine is reduced to give phenoxyselenine in boiling acetone with the formation of bromoacetone (H. D. K. Drew, J. Chem. Soc., 1927, 511).
4) N. W. Pideswell and J. D. McCullough, J. Am. Chem. Soc., 79, 1031 (1957).
5) R. N. Loeppky and D. C. K. Chang, Tetrahedron Lett., 5415 (1969).

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