

S_H2 REACTIONS OF SELENOSULFIDES WITH CARBON RADICALS

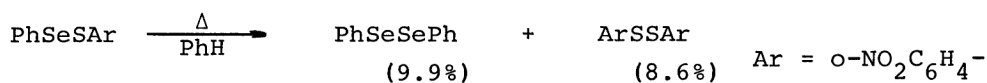
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o-Nitrophenyl phenylselenyl sulfide suffered S_H2 attack by carbon radicals on selenium atom to give selenide and thiyl radical; the relative rate constant of the selenosulfide with phenyl radical was compared with those of the other selenium compounds.

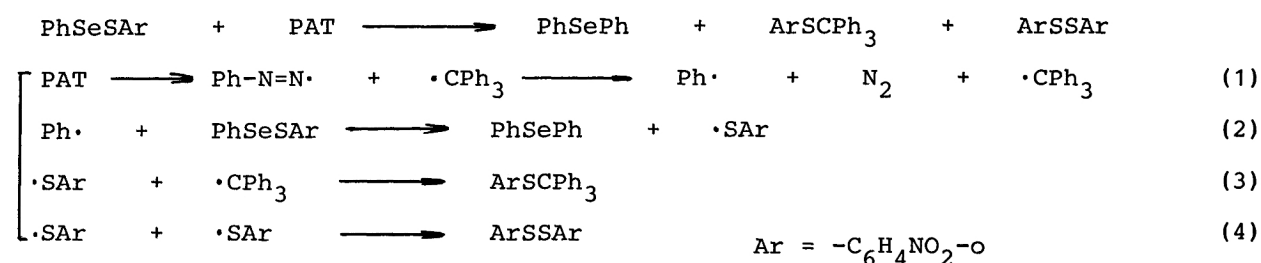
It was found that the facile addition of selenosulfonate ($PhSeSO_2Ar$) to olefins or acetylenes took place by radical chain mechanism.¹⁾ However, structurally analogous thiosulfonate ($ArSSO_2Ar$) did not react with olefins or acetylenes to give the adducts. The difference should be attributed to the different reactivity of selenium and sulfur in S_H2 reaction with carbon radicals; reactivity of selenosulfonate in S_H2 reaction with carbon radical should be much higher than that of thiosulfonate. Thus, we became interested in the S_H2 reaction of organic selenium compounds with carbon radicals. Recently, Russell and Tashtoush reported that diphenyl diselenide exhibited very high reactivity compared to diphenyl disulfide in S_H2 reaction with Δ -hexenyl radical.²⁾ In this paper, we wish to report the S_H2 reaction of selenosulfide ($PhSeSAr$) with several carbon radicals.

Generally, it was difficult to isolate selenosulfide from disproportionated products disulfide and diselenide, and *o*-nitrophenyl phenylselenyl sulfide ($PhSeSC_6H_4-NO_2-o$ **1**) was an only known selenosulfide to be purely isolated.³⁾ So we examined the S_H2 reaction of **1** at first. The selenosulfide **1** was thermally stable; even after 22 h's heating in benzene under reflux, only less than 10% of disproportionated products were detected.



However, the decomposition of **1** was accelerated very much by the addition of radical source, such as phenylazotriphenylmethane (PAT). When an equimolar amount

of PAT was added to a solution of 0.1 mol dm⁻³ of 1 in benzene and the resulted solution was heated under reflux, the decomposition of 1 was completed after 1 h to give a mixture of diphenyl selenide, di-o-nitrophenyl disulfide, and phenyl triphenylmethyl sulfide. The reaction mechanism was shown in Scheme 1.



Scheme 1.

Phenyl radical, produced by the decomposition of PAT, attacks on selenium of 1 to expel thiyl radical (Eq. 2). The released thiyl radical recombines with triphenylmethyl radical to give o-nitrophenyl triphenylmethyl sulfide (Eq. 3) or dimerizes to the disulfide (Eq. 4). o-Nitrophenyl phenyl sulfide, which was the expected product of the S_H2 reaction of phenyl radical with 1 on sulfur atom, was not detected. S_H2 reaction can be subdivided into those which are direct synchronous displacement and those which are stepwise with a true radical intermediate of finite life time.⁴⁾ ESR spectra assigned to the σ* selenuranyl radicals R₂Se[•]-SCF₃ (R = alkyl or aryl) have been reported.⁵⁾ Thus, it is reasonable to assume that the S_H2 reaction of 1 with phenyl radical proceeds by stepwise via selenuranyl radical as an intermediate. High selectivity of selenium atom compared to sulfur atom against S_H2 attack to 1 by phenyl radical may be explained by the higher stability of selenuranyl radical compared to sulfuranyl radical.

The reactions using t-butyl phenylazo sulfone (Ph-N=N-SO₂-Bu-t) and azobisisobutyronitrile (AIBN) as radical sources were also examined. The results were summarized in Table 1. t-Butyl and 2-cyano-2-propyl radicals also attacked on selenium atom selectively.

To confirm the reaction mechanism shown above, CIDNP studies were also carried out. ¹³C-CIDNP spectra observed in thermal decomposition of t-butyl phenylazo sulfone with or without 1 were shown in Fig. 1. During the decomposition of azo sulfone in the presence of 1, strong emission signal of C₁ in diphenyl selenide and enhanced absorption signal of quaternary carbon atom of t-butyl phenyl selenide were observed besides of the signals observed in the thermal decomposition of azo sulfone alone. According to the Kaptein's rule, cage escaped phenyl and t-butyl

Table 1. Products for Induced Decomposition of 1 by Carbon Radicals

Radical sources	Reaction time/ h	Products (Isolated yield / %) ^{b)}	
PAT	1	PhSePh (77.8)	ArSCPh ₃ (53.4)
		Ph ₃ CH (12.3)	
		Ph ³ -Ph (12.3)	
		Recovered <u>1</u> (24.5)	ArSSAr ₃ (11.8)
Ph-N=N-SO ₂ -Bu-t	1	PhSePh (39.3)	ArSSAr (29.1)
		PhSeBu-t (18.7)	
		Recovered <u>1</u> (23.0)	
AIBN	22	PhSeSePh (24.9)	ArSSAr (37.9)
		Me ₂ (CN)CSePh (29.3)	
		Recovered <u>1</u> (28.7)	

a) Ar = C₆H₄NO₂-o. b) Based on 1. c) These compounds (*1) and (*2) could not be separated each other. Ratio was determined by GC (*1) or ¹H-NMR (*2).

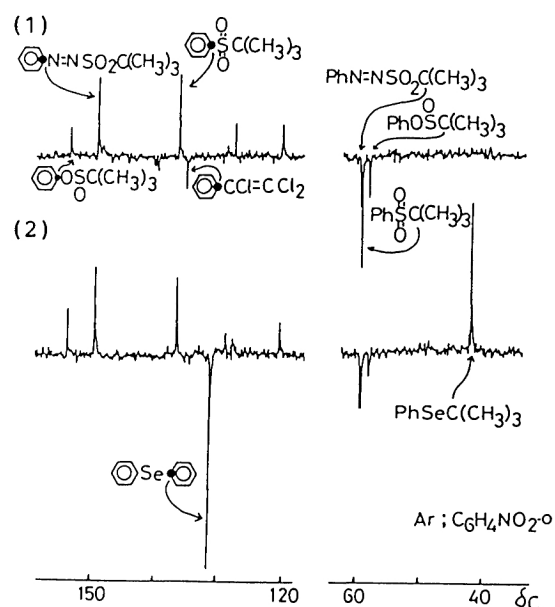
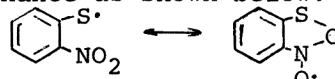


Fig. 1. CIDNP spectra observed in thermal decomposition of t-butyl phenylazo sulfone (1) without, (2) with selenosulfide 1 in CCl₂=CCl₂.

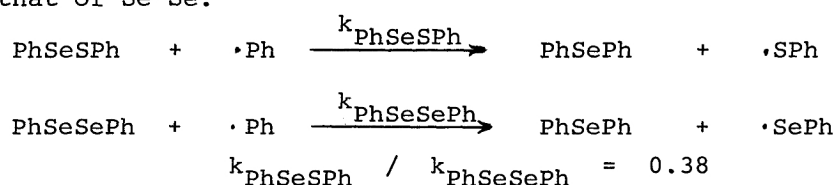
Thus, we examined the reactivity of phenyl phenylselenyl sulfide (PhSeSPh 2). As has been mentioned before, 2 could not be isolated in pure state from the disproportionated products, diselenide and disulfide. However, resolved peaks due to disulfide, selenosulfide, and diselenide could be observed by GC using 10% SE-30 2 m column and each peaks were identified by GC-MS. Thus, we could determined the relative rate constant for S_H2 reaction of 2 with phenyl radical

radicals should exhibit opposite signs to recombination products in solvent cage, namely sulfinic ester, sulfone, and azo sulfone. As shown in Fig. 1, phenyl carbon of diphenyl selenide exhibits emission signal while phenyl carbon of t-butyl sulfone, cage product, shows enhanced absorption, and quarternary carbon atom of t-butyl in t-butyl phenyl selenide exhibits enhanced signal in contrast to the emission signal of t-butyl phenyl sulfone. Thus, CIDNP result is consistent with proposed mechanism.

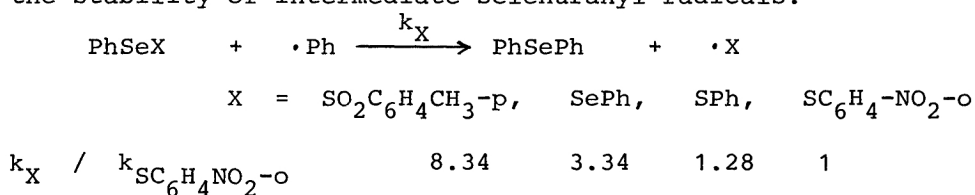
The reaction of selenosulfide 1 could be a special case because the released o-nitro-benzenethiyl radical may be stabilized by the resonance as shown below.



to that of diphenyl diselenide by use of GC. A solution of a mixture of 2 diphenyl diselenide, and diphenyl disulfide in benzene in the presence of PAT was heated at 80 °C, and the rate of decrease of 2 and diselenide was monitored by GC. Relative rate of selenosulfide to diselenide was determined to be about 0.4. This reactivity difference may be attributed to the higher bond energy of Se-S than that of Se-Se.



Relative rate constants for the S_H2 reactions of various selenium compounds with phenyl radical were also determined in a similar way. The highest reactivity was observed in the case of selenosulfonate. Assuming the first step to form selenuranyl radicals as the rate determining step, the relative rates may reflect the stability of intermediate selenuranyl radicals.



References

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