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Novel Method for Electrophilic Selenenylation Using Diselenide with Nitrobenzenesulfonyl Peroxide

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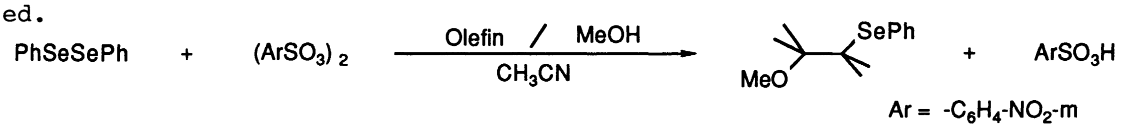
Diphenyl diselenide could be readily converted into cationic selenenylating reagent by treating with m-nitrobenzenesulfonyl peroxide, and the intermediate was reacted with olefins in the presence of methanol, phenol, or electron-rich benzenes in one pot to afford methoxy-, phenoxy-, or arylselenenylated compounds, respectively.

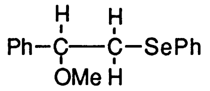
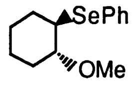
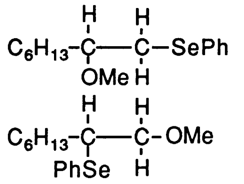
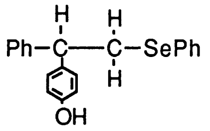
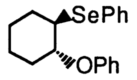
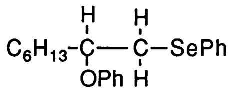
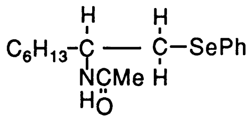
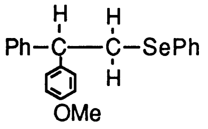
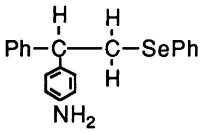
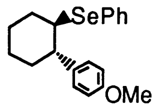
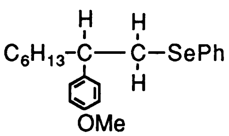
We have been exploring novel methods for introduction of various important functional groups into aromatic rings or olefins using peroxides.[1,2] We are currently interested in the conversion of stable substrates into cationic reagents using peroxides.[2] In the course of the study, we found that diphenyl diselenide, which is stable and easy to handle, could be converted into very reactive cationic selenenylating reagent with m-nitrobenzenesulfonyl peroxide (m-NBSP), and the results will be described in this communication.

When m-NBSP[3] (0.5 mmol) was added to a solution of diphenyl diselenide (0.5 mmol) in 20 ml acetonitrile, the color of the solution turned reddish brown. The resulting solution was stirred at 0 °C for 1 h and then a solution of an olefin (1.1 mmol), such as styrene, cyclohexene, or octene, in 5 ml methanol was added. The reaction mixture was further stirred for additional 3 h. Methoxyselenenylations of olefins occurred in good yield (Table 1; run 1, 2, 3) and with high regioselectivity (Markownikoff type addition Table 1; run 1, 3) and stereoselectivity (trans addition Table 1; run 2). The methoxyselenenylation did not occur when t-butyl hydroperoxide or benzoyl peroxide were used.



When phenol was used as a nucleophile, unexpectedly phenol added to the double bond of styrene at the para position (arylselenenylation Table 1; run 4), whereas phenoxyselenenylation occurred when cyclohexene or octene was employed (Table 1; run 5, 6). We further examined the reactions of styrene with diphenyl diselenide and m-NBSP in the presence of various benzenes as nucleophiles. When electron-rich benzenes, such as anisole or aniline, were

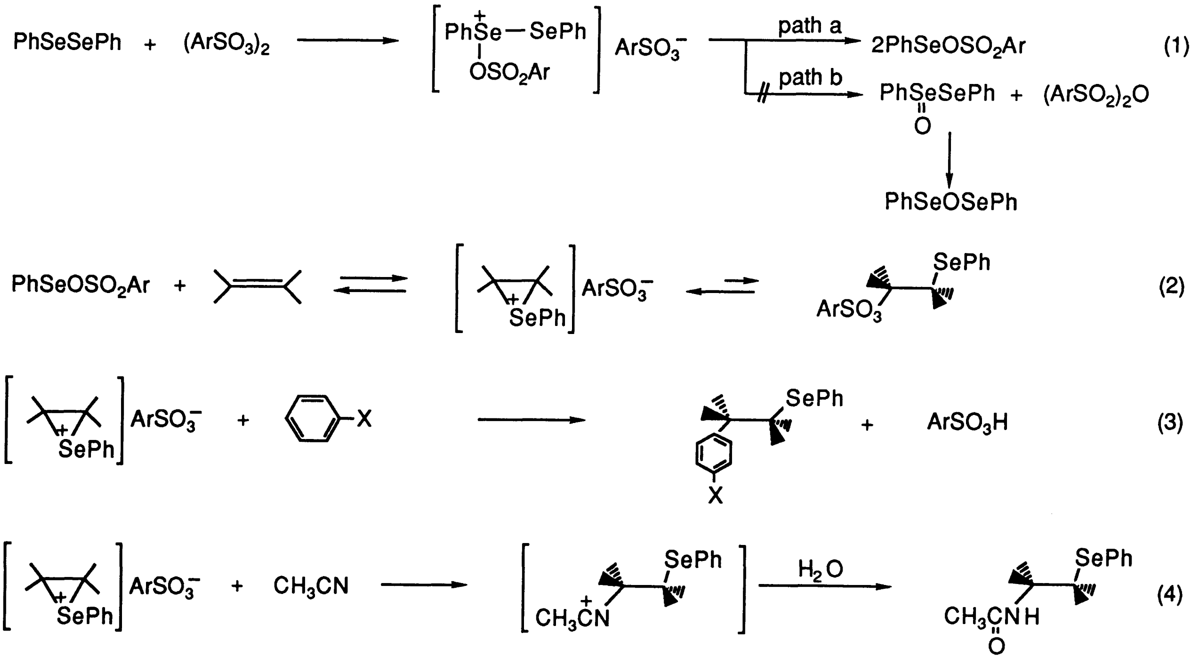
Table 1. Oxy- and arylselenenylation of olefins by diphenyl diselenide with *m*-NBSP

Run	Olefin	Method[a)]	Solvent	Nucleophile	Product / %[b)]	
1	styrene	A	CH_3CN	MeOH	 $\mathrm{Ph-\underset{OMe}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-SePh}$	98
2	cyclohexene	A	CH_3CN	MeOH		92
3	octene	A	CH_3CN	MeOH	 $\mathrm{C_6H_{13}-\underset{OMe}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-SePh}$ $\mathrm{C_6H_{13}-\underset{PhSe}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-OMe}$	83[c)]
4	styrene	B	CH_3CN	PhOH		78
5	cyclohexene	B	CH_3CN	PhOH		38
6	octene	B	CH_3CN	PhOH	 $\mathrm{C_6H_{13}-\underset{OPh}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-SePh}$	25
				CH_3CN[d)]	 $\mathrm{C_6H_{13}-\underset{\underset{H\ O}{NCMe}}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-SePh}$	16
7	styrene	A	CH_3CN	PhOMe		96
8	styrene	B	CH_3CN	$PhNH_2$		33
9	cyclohexene	A	CH_3NO_2	PhOMe		30
10	octene	A	CH_3NO_2	PhOMe		53

a) Method A; To the resulting solution of diselenide (0.5 mmol) with *m*-NBSP (0.5 mmol) in 20 ml of solvent, 1.1 mmol of olefin in nucleophile (5 ml) was added. Method B; To the resulting solution, olefin (1.1 mmol) and then nucleophile (10 mmol of phenol or 2 mmol of aniline) were added. b) Isolated yield. All the products gave satisfactory spectral data. c) Obtained as a mixture of two isomers. The ratio of 1-benzeneselenenyl / 2-benzeneselenenyl was determined to be 4.1 by GC. d) Solvent acetonitrile reacted as nucleophile.

used, arylselenenylations occurred (Table 1; run 7, 8). However, toluene or benzene did not undergo arylselenenylation under similar conditions. The anisylselenenylation of cyclohexene and octene were also examined, but amidoselenenylation occurred when the reaction was performed in acetonitrile; solvent acetonitrile reacted as nucleophile in preference to anisole. Anisylselenenylations of cyclohexene and octene could be achieved when nitromethane was used as solvent (Table 1; run 9, 10).

It is known that the reaction of diphenyl diselenide with peroxide, such as t-butyl hydroperoxide, usually gives selenenic anhydride (PhSeOSePh).[4)] However, oxyselenenylation does not occur in the reaction of benzenselenenic anhydride with styrene in the presence of methanol. Thus, we propose the formation of benzeneselenenyl arenesulfonate ($PhSeOSO_2Ar$) in the reaction of diselenide with m-NBSP (path a of Eq. 1 in Scheme 1). Since the nucleophilicity of sulfonate is very low, the oxidation of selenium may not occur (path b of Eq. 1 in Scheme 1). The benzeneselenenyl group in selenenyl sulfonate acts as an electrophile due to the effect of strong electron-withdrawing sulfonyloxy group. Methoxyselenenylation is well known as one of the reactions of electrophilic selenenylating reagent with olefins in the presence of methanol via episelenonium ion.[5)] The trans addition observed in this methoxyselenenylation of cyclohexene involves the formation of episelenonium salt. However, arylselenenylation of olefin has never been reported in the literature. The selenenyl sulfonate reacts with olefin to give episelenonium salt (Eq. 2 in Scheme 1). Although episelenonium salt usually exists in equilibrium with its adduct,[6)] the episelenonium arenesulfonate did not give the adduct, probably because the counter anion, m-



Scheme 1.

nitrobenzenesulfonate, is a very stable and very weak nucleophile (Eq. 2 in Scheme 1). The cations which have stable counter anions, such as trifluoromethanesulfonate, often show high and unique reactivities.[6,7) Therefore, the episelenonium arenesulfonate is expected to react with various nucleophiles which are added to the reaction systems; the episelenonium ion may attack benzene ring electrophilically to give arylselenenylated olefins (Eq. 3 in Scheme 1). Amidoselenenylation from episelenonium trifluoromethanesulfonate was reported to proceed by the attack of the nitrogen atom of acetonitrile on the episelenonium ion.[6) Under our reaction conditions amidoselenenylations occurred, and this also suggests the generation of episelenonium ion (Eq. 4 in Scheme 1). Thus, episelenonium m-nitrobenzenesulfonate was found to be readily produced in the reaction of diphenyl diselenide with m-NBSP in the presence of olefins.

Oxidative cleavage of diphenyl diselenide by halogens, such as bromine or chlorine, is one of the most important and general methods for the formation of electrophilic selenenylating reagents (benzeneselenenyl halide).[8) In this study we found that diphenyl diselenide could be readily converted into very reactive electrophilic selenenylating reagent, probably benzeneselenenyl arenesulfonate, by the use of m-NBSP. The selenenyl sulfonate reacted with olefins to give episelenonium arenesulfonate, which is expected to react with various nucleophiles. Thus, the reaction described in this paper is very attracive and potentially useful in organic synthesis.

References

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