Oxyselenation of Olefins by the Use of Aryl or Alkyl Selenocyanates and Copper or Nickel Halides

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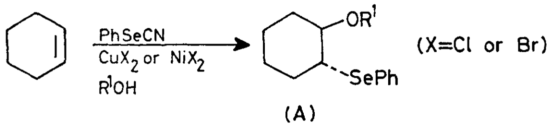
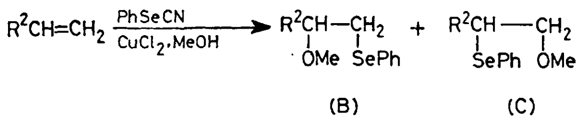
Summary Reaction of olefins with aryl or alkyl selenocyanates in alcohol, water, or acetic acid in the presence of copper or nickel(II) halides produces the corresponding β-oxy selenides in high yields.

OXYSELENATION is an effective method for introducing selenium to produce organoselenium compounds, the chemistry of which is of current interest.[1] We now report the ready oxyselenation of olefins by the use of aryl or alkyl selenocyanates with a copper or nickel halide.

In a typical reaction, solid copper(II) chloride (5 mmol) was added to a methanol (10 ml) solution containing cyclohexene (10 mmol) and phenyl selenocyanate (5 mmol) at 65 °C and the mixture was kept at this temperature for 0·5 h. G.l.c. analysis after the usual work-up revealed the formation of *trans*-2-methoxycyclohexyl phenyl selenide [(A; R^1 = Me) 5 mmol; 100%; b.p. 151—153 °C at 8 Torr] as the sole product. The reaction proceeded even with a catalytic amount of copper(II) chloride [*i.e.*, with 0·25 mmol of $CuCl_2$ and 2 mmol of phenyl selenocyanate, 1·94 mmol of (A; R^1 = Me) was formed], while no reaction occurred without the addition of copper(II) chloride. Application to other olefins such as styrene, hex-1-ene, and oct-1-ene afforded the corresponding 2-methoxyalkyl phenyl selenide [(B) and/or (C)] in high yield. Here, it was found that attack of selenium on the terminal carbon atom is completely selective in the case of styrene and is favoured in the cases of other terminal olefins to give (B), and also that (C) isomerizes to (B) with longer reaction times in the latter cases. Typical results are shown in the Table.





Similar treatment of cyclohexene in other alcohols, $CHCl_3$–AcOH, and tetrahydrofuran–H_2O gave the corresponding selenides (A; R^1 = Et, Pr^i, MeCO, and H) in 50—100% yield. The last compound, *trans*-2-hydroxycyclohexyl phenyl selenide, was identical with an authentic sample prepared from cyclohexene oxide, phenyl selenocyanate, and sodium borohydride.[2,3] The reactions with alkyl selenocyanates such as n-hexyl and benzyl in methanol also proceeded smoothly to afford the corresponding β-methoxy selenide.

Of the many metal salts other than copper(II) chloride examined, copper(II) bromide, copper(I) chloride, and nickel(II) bromide and chloride showed similar activity to copper(II) chloride, while the chlorides of Mn^{II}, Fe^{II}, Zn^{II},

TABLE.[a] Reaction of olefins with PhSeCN

Olefin	Temp./°C	Time/h	Product[b]	% Yield	Isomer ratio of (B) to (C)
Cyclohexene	65	0·5	(A; R^1=Me)	100	
Cyclohexene	27	3	(A; R^1=Me)	80	
Styrene	65	0·5	(B; R^2=Ph)	87	
Styrene	25	5	(B; R^2=Ph)	87	
Hex-1-ene	65	0·5	(B and C; R^2=Bu^n)	95	82 : 18
Hex-1-ene	65	3	(B and C; R^2=Bu^n)	94	90 : 10
Oct-1-ene	25	15	(B and C; R^2=C_6H_{13}[c])	88	83 : 17
Oct-1-ene	65	0·5	(B and C; R^2=C_6H_{13})	94	83 : 17
Oct-1-ene	65	10	(B and C; R^2=C_6H_{13})	93	93 : 7

[a] Olefin (10 mmol), PhSeCN (5 mmol), $CuCl_2$ (5 mmol), and MeOH (10 ml). [b] All new compounds gave satisfactory analytical and spectral data. [c] C_6H_{13} = n-hexyl.

Ag^I, Cd^{II}, Hg^{II} and Hg^I, and Tl^{III} and Tl^I were almost ineffective. Since the regiospecificity in the products suggests electrophilic attack of the PhSe group on the olefins, the role of the metal salts which were effective seems to be the removal of cyanide ion from phenyl selenocyanate by co-ordination. In fact, the yield of selenide was always lower if the pyridine adduct of these metal salts was used {*i.e.*, only 9% of (A; R = Me) was obtained by the use of $[CuCl_2(C_5H_5N)_2]$ at 65 °C for 0·5 h}, probably because the co-ordination site is blocked.

The oxyselenation described here provides another method for organic synthesis using the easily accessible aryl[3,4] and alkyl selenocyanates.

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