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ACETOXYSELENATION: REACTION OF OLEFINS WITH DIPHENYL DISELENIDE AND CUPRIC ACETATE

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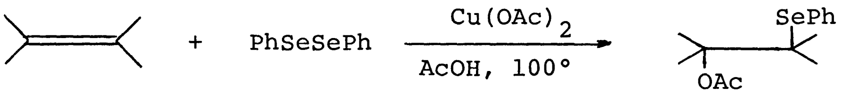
In the presence of cupric acetate, diphenyl diselenide was found to react with olefins in acetic acid to afford 2-acetoxyalkyl phenyl selenide(1). The similar reaction proceeded by use of a catalytic amount of cupric acetate in the presence of oxygen. Formation of benzeneselenenyl acetate(PhSeOAc) as an intermediate is suggested.

There has been much interest in oxyselenation reaction because of their usefulness in synthesis[1)]. Since we had reported the acetoxyselenation of olefins[2a)], considerable efforts have been devoted to study on the further development of oxyselenation of olefins[2b,c)].

We report here a new and convenient method of acetoxyselenation of olefins which includes the reaction of diphenyl diselenide with cupric acetate as shown in eq 1.



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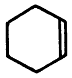
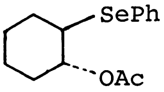
(1)

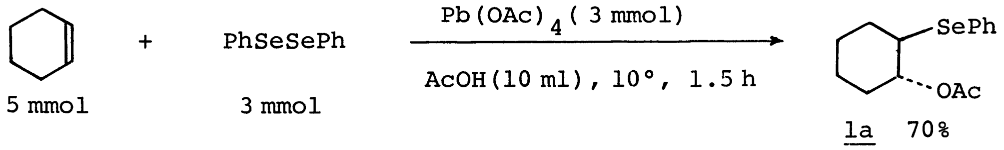
The following procedure for the preparation of trans-2-acetoxycyclohexyl phenyl selenide(1a) is representative: cyclohexene(0.41g, 5 mmol) was added to acetic acid(10 ml) solution containing cupric acetate(1.09g, 6 mmol) and diphenyl diselenide(0.94g, 3 mmol) at room temperature with vigorous stirring, and the mixture was heated at 100° for 1.5 h during which period the colour turned from dark green to yellow. After cooling, the mixture was diluted with ether(40 ml) and the yellow precipitates were filtered off. Distillation of the filtrate afforded trans-2-acetoxycyclohexyl phenyl selenide(1a) (1.03g, 69%). The structure of the product(1a) was established by its NMR, IR and Mass spectra. By this method, various selenides(1) were prepared as shown in Table 1. An electron deficient olefin, methyl acrylate, did not react.

Table 1. Acetoxyselenation of Olefins

Olefin	Time (h)	Product 1[a)] (ratio)[b)]	Yield(%)[c)]
	1.5	 1a	69
	2	n-$C_4H_9CH(OAc)CH_2SePh$, n-$C_4H_9CH(SePh)CH_2OAc$ 1b (80 : 20) 1c	70
	2	n-$C_6H_{13}CH(OAc)CH_2SePh$, n-$C_6H_{13}CH(SePh)CH_2OAc$ 1d (67 : 33) 1e	72
	2	$C_2H_5CH(OAc)CH(SePh)C_2H_5$ 1f	37[d)]

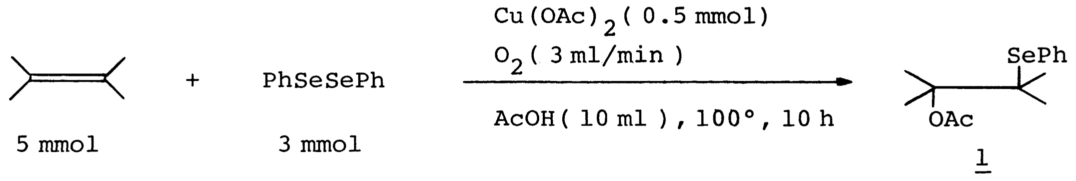
a) All compounds were characterized by direct comparison with authentic sample.
b) Ratio determined by NMR measurement. c) Isolated yield.
d) Sodium acetate(0.5 mmol) was added into the reaction system.

When lead tetraacetate, instead of cupric acetate, was used stoichiometrically in the reaction of cyclohexene with diphenyl diselenide, the reaction proceeded under mild conditions to give 1a in comparative yield as shown in eq 2[3)].



(2)

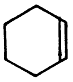
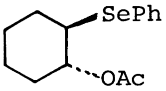
Furthermore, we found that cupric acetate can be used catalytically when oxygen is introduced to the reaction system.[4)] For example; to a solution of diphenyl diselenide(0.94g, 3 mmol) and a catalytic amount of cupric acetate (0.09g, 0.5 mmol) in 10 ml of acetic acid was added cyclohexene(0.41g, 5 mmol) at room temperature, and oxygen (3 ml/min) was bubbled into the mixture at 100° for 10 h. The mixture was then diluted with ether (40 ml). Filtration of the precipitates deposited and removal of the solvent gave a yellow oil, which was distilled under reduced pressure to give trans-2-acetoxycyclohexyl phenyl selenide (1a) (1.12g, 75 %).



(3)

The results are shown in Table 2.

Table 2. Cupric Acetate Catalyzed Acetoxyselenation of Olefins

Olefin	Product 1 (ratio)[a]	Yield (%)[b]
	 1a	75
	n-$C_6H_{13}CH(OAc)CH_2SePh$ 1d (82 : 18) n-$C_6H_{13}CH(SePh)CH_2OAc$ 1e	59
	$C_2H_5CH(OAc)CH(SePh)C_2H_5$ 1f	32[c]

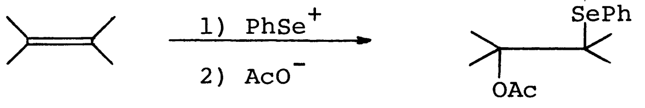
a) Ratio determined by NMR measurement. b) Isolated yield.
c) This reaction was carried out under atmosphere of oxygen.

Although mechanistic investigation has not been carried out yet, a plausible reaction path for these reactions is suggested as in the scheme I.

Scheme I

$$PhSeSePh + Cu^{++} \longrightarrow PhSe\cdot + Cu^{+} + PhSe^{+} \quad (4)$$

$$PhSe\cdot + Cu^{++} \longrightarrow PhSe^{+} + Cu^{+} \quad (5)$$



(6)

The electrophilic species ($PhSe^+$) is thought to be generated by the reaction between diphenyl diselenide and cupric acetate. In the catalytic reaction, cupric ion may be regenerated by the oxidation of cuprous ion with oxygen. These reactions may provide a new convenient method of acetoxyselenation of olefins.

References

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2. a) N. Miyoshi, S. Furui, S. Murai, and N. Sonoda, J.C.S., Chem. Commun., 1975, 293; b) N. Miyoshi, S. Murai, and N. Sonoda, Tetrahedron Lett., 1977, 851; c) N. Miyoshi, Y. Takai, S. Murai, and N. Sonoda, Bull. Chem. Soc. Japan, 51, 1265(1978).
3. The reaction of lead tetraacetate and diphenyl disulfide with olefins give corresponding acetoxysulfenylated products, see; B. M. Trost, M. Ochiai, and P. G. Mcdougal, J. Am. Chem. Soc., 100, 7103(1978).
4. Similar sulfenylation using diphenyl disulfide was unsuccessful when cupric acetate was used as the catalyst or as the stoichiometric reactant.

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