

Catalytic Conversion of Alkenes into Allylic Ethers and Esters using Diselenides having Internal Tertiary Amines

Michio Iwaoka and Shuji Tomoda*

Department of Chemistry, College of Arts and Sciences, The University of Tokyo, Komaba, Meguro-ku, Tokyo 153, Japan

2,2'-Diselenobis(*N,N*-di[2-(2-pyridyl)ethyl]benzylamine) **1** with copper(II) nitrate or 2,2'-diselenobis(*N*-cyclohexyl-*N*-methylbenzylamine) **2** catalyses the conversion of alkenes **3** into oxygenated allylic compounds **4** both in methanol and in acetic acid in the presence of sodium persulfate as an oxidizing agent.

The two-step conversion of alkenes into oxygenated allylic compounds using electrophilic selenium reagents *via* addition and oxidative *syn*-elimination¹ has been extensively applied to selective organic synthesis.² It was previously demonstrated by Torii *et al.* in the electrochemical reaction³ that the conversion could be made catalytic with respect to the selenium reagent if selenenic acid ($-\text{SeOH}$), which was generated as a by-product after the oxidative elimination of the selenium moiety, could be captured by another molecule of alkene before its inactivation *via* oxidative disproportionation into selenenic anhydride and/or seleninic acid. However, no preparative approach to catalytic reactions has been reported to date owing to the rapid inactivation of selenenic acid in the presence of an oxidizing agent. We report here on the preliminary results of developing the catalytic conversion of alkenes into allylic ethers or esters by using 2,2'-diselenobis(*N,N*-di[2-(2-pyridyl)ethyl]benzylamine) **1** or 2,2'-diselenobis(*N*-cyclohexyl-*N*-methylbenzylamine) **2**⁴ as a

catalyst in the presence or the absence of copper(II) nitrate trihydrate. To the best of our knowledge, this is the first chemical process of catalytic conversion of alkenes into allylic compounds using organoselenium reagents.⁵

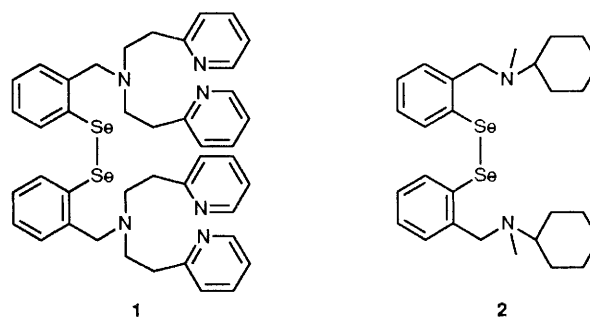


Table 1 Conversion of alkenes **3** into allylic ethers or esters **4** catalysed by **1** or **2**^a

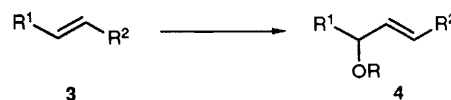
Alkene 3	Product 4	Method ^b	Solvent (ROH) ^c	Yield of 4 ^d (%)
		A	MeOH	285 (38)
		A	AcOH	324 (37)
		A	MeOH	232 (29)
		A	AcOH	402 (51)
		B	MeOH	193 (28)
		B	AcOH	595 (62)
		B	AcOH	551 ^e (55)
		A	MeOH	0 ^f
		A	AcOH	457 (46)
		A	MeOH	166 (26)
		A	AcOH	414 (51)

^a In all cases sodium persulfate was used as an oxidizing agent and molecular sieve 3A (0.2 g) was added to the reaction mixture as a desiccant; the reaction procedure is given in the text. ^b Method A: **1** was used as a catalyst in the presence of copper(II) nitrate trihydrate. Method B: **2** was used as a catalyst in the absence of copper(II) nitrate trihydrate. ^c MeOH = methanol; AcOH = acetic acid. ^d Determined by gas chromatography with respect to the amounts of the selenium catalysts. Values in parentheses were actual yields (%) of **4** with respect to **3** considering the yield of **3** recovered. ^e In the presence copper(II) nitrate trihydrate. ^f Only unidentified volatile products were formed.

In modelling such a catalytic system, the stabilization of selenenic acid as well as selection and/or modification of an oxidizing agent seemed essential. In a previous paper⁴ we reported on the strong interaction between an electrophilic selenium and an internal tertiary amine. With the hope that the stabilizing interaction would interrupt the disproportionation of a selenenic acid intermediate, diselenides having intramolecular tertiary amines were applied to the catalytic conversion of alkenes **3** into allylic ethers or esters **4** (Scheme 1).

Diselenide **1** was synthesized by the coupling reaction between 2,2'-diselenobis(benzyl chloride)⁴ and bis[2-(2-pyridyl)ethyl]amine⁶ in refluxing benzene in the presence of triethylamine in 37% yield. Catalytic reactions were carried out as follows: **1** (0.1 mmol) and copper(II) nitrate trihydrate (0.1 mmol) were dissolved in methanol or acetic acid (3 ml) and the mixture was stirred at room temperature for 30 min.† Then an excess amount of alkene **3** (1.0 mmol) and an oxidizing agent (1.0 mmol) were successively added to the solution. After stirring for 7 d, the mixture was filtered and the filtrate extracted with dichloromethane. Polymeric by-products were removed by column chromatography (dichloromethane as eluent), then the yields of **4** and **3** recovered were determined by gas chromatography.

Initially hydrogen peroxide was utilized as an oxidizing agent. The desired product **4** was, however, obtained only in modest yield for various alkenes (8–32% with respect to **1**). After screening various oxidizing agents such as inorganic persulfate, perchlorate and periodate salts, it was found that the reaction proceeded catalytically when sodium persulfate was used as the oxidizing agent. The most efficient conversion



Scheme 1 Reagents and conditions: cat. **1** or **2** + Cu(NO₃)₂·3H₂O, Na₂S₂O₈, molecular sieve (3 Å), ROH, room temp., 7 d, (R = Me or Ac)

was achieved when molecular sieve 3A was added to the reaction mixture. This may suggest that removal of the water, formed as the reaction proceeds, seems essential for the smooth addition of selenenic acid to the alkene. The yields of **4** with respect to **1** are listed in Table 1 for various alkenes; in each case unreacted **3** was recovered as an almost single volatile material.

The results clearly show that **1** with copper(II) nitrate (method A) indeed catalyses the conversion of various alkenes **3** into the corresponding allylic ethers or esters **4**. The reaction uniformly proceeds more efficiently in acetic acid than in methanol. The reaction mechanism seems as follows: An electrophilic selenium species, generated by the oxidation or disproportionation of **1**, reacts with **3** to produce an oxy-selenenylated product followed by oxidation. The selenoxide thus produced forms **4** and selenenic acid, which reacts with **3** once again. Copper(II) nitrate may be involved chiefly in the initial step of the catalytic reaction, the oxidative cleavage of an Se–Se bond.

When **2**⁴ was used as a catalyst instead of **1** (method B), the efficiency of the reaction increased [(*E*)-oct-4-ene in acetic acid]. In this case the catalytic reaction also proceeded in the absence of copper(II) nitrate: the highest yield (595% with respect to **2**) was achieved. In methanol, however, the yield obtained by using method B (193%) was slightly reduced from that (232%) obtained according to method A for (*E*)-oct-4-ene. Although the reaction is sluggish presumably owing to low solubility of sodium persulfate and turnovers achieved are not satisfactory as a preparative method at present, it should be mentioned that the highest turnover (5.95) is comparable to that obtained in the electrochemical catalytic process of

† At this stage the solution turned dark-green. In the UV spectrum the absorption bands at 257, 262, and 268 nm reduced in intensity with increasing amount of copper(II) ion presumably owing to coordination of pyridine moieties to the metal cation. During this process, a new broad band formed around 305 nm. An isosbestic point was observed at 282 nm until 1.0 mol equiv. amount of copper(II) ion was added. These observations are consistent with the formation of 1 : 1 complex of the ligand and Cu^{II} in methanol.

similar transformations using organoselenium reagents.³ We are now attempting to improve the efficiency of the catalyst by modifying the diselenide and/or the oxidizing agent; the results will be disclosed in due course.

This work is supported by Grants in Aid for Scientific Research offered by the Ministry of Education, Culture and Science (Nos. 02230209, 02247204, 03233204, 03453026).

Received, 24th April 1992; Com. 2/02124B

References

- 1 K. B. Sharpless and R. F. Lauer, *J. Org. Chem.*, 1974, **39**, 429.
 - 2 C. Paulmier, *Selenium Reagents and Intermediates in Organic Synthesis*, Pergamon Press, Oxford 1986; K. C. Nicolaou and N. A. Petasis, *Selenium in Natural Products Synthesis*, CIS, 1984; D. L. J. Clive, *Tetrahedron*, 1978, **34**, 1049; H. J. Reich, *Acc. Chem. Res.*, 1979, **12**, 22; D. Liotta, *Acc. Chem. Res.*, 1984, **17**, 28.
 - 3 S. Torii, K. Uneyama, M. Ono, and T. Bannou, *J. Am. Chem. Soc.*, 1981, **103**, 4606.
 - 4 M. Iwaoka and S. Tomoda, *Phosphorus Sulfur Silicon Relat. Elem.*, 1992, **67**, 125.
 - 5 A similar chemically catalytic process of ketone dehydrogenation using diphenyl diselenide or benzeneseleninic anhydride and iodoxybenzene as an oxidizing agent has been reported: D. H. Barton, C. R. A. Godfrey, J. W. Morzycki and W. B. Motherwell, *J. Chem. Soc., Perkin Trans. 1*, 1981, 1947.
 - 6 L. E. Brady, M. Freifelder and G. R. Stone, *J. Org. Chem.*, 1961, **26**, 4757.
-