

Cyanoselenenylation of Olefins[†]

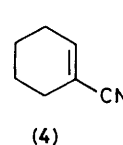
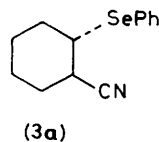
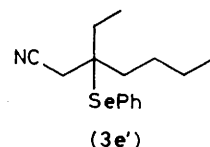
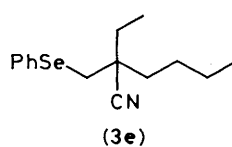
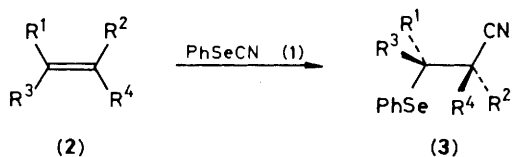
Shuji Tomoda,* Yoshito Takeuchi, and Yujiro Nomura

Department of Chemistry, College of General Education, The University of Tokyo, Komaba, Meguro-ku, Tokyo 153, Japan

The reaction of simple olefins with phenyl selenocyanate in the presence of a Lewis acid provided 2-phenylseleno carbonitriles, the vicinal cyanoselenenylation products, stereoselectively in excellent yields.

Despite many examples of addition reactions of organoselenium reagents across unactivated carbon-carbon double bonds,¹ cyanoselenenylation of simple olefins has hitherto not been reported. We now report that phenyl selenocyanate (**1**) undergoes efficient vicinal cyanoselenenylation with simple olefins in the presence of a Lewis acid catalyst.

Although (**1**), a chromatographically stable liquid,² reacts rapidly with nucleophilic olefins, such as enamines, without catalyst,³ it is completely inert toward unactivated olefins. However, it was expected that (**1**) might react with simple olefins (**2**) in the presence of an appropriate catalyst to afford 2-phenylselenocarbonitriles (**3**). After thorough screening studies of catalysts, Lewis acids, such as SnCl₄, BF₃, and AlCl₃ were found to be more effective⁴ than the soft transition metal salts which have been frequently employed to activate organoselenium compounds.⁵ Of these Lewis acid catalysts, the best results were obtained with SnCl₄ (Table 1). Thus, cyclohexene (**2a**) reacted with (**1**), in the presence of 1 mol. equiv. SnCl₄ in dry dichloromethane, within 4 h at 15 °C under argon to provide a single stereoisomer of 2-phenylseleno-cyclohexanecarbonitrile (**3a**) in 96% yield after column chromatography on silica gel. Its structure was elucidated by spectroscopic methods and elemental analysis. The presence of a cyano group was clearly indicated by i.r. (2245 cm⁻¹, sharp medium band) and ¹³C n.m.r. spectroscopy (δ 120.9 p.p.m.).



The *trans*-stereochemistry between the phenylseleno and cyano groups was suggested by a large coupling constant (*J* 9.0 Hz) between H-1 (δ 2.53) and H-2 (δ 3.16) in the ¹H n.m.r. spectrum.

[†] For Part 4 of the series Organoselenium Chemistry, see ref. 5(b).

Table 1. Reactions of olefins (2) with phenyl selenocyanate (1).^a

Compound	R ¹	R ²	R ³	R ⁴	Catalyst	% Yield ^b	(3)	I.r. ^d ν(C≡N)/cm ⁻¹
							¹³ C N.m.r. ^c δ(C=N)/p.p.m.	
(2a)	-[CH ₂] ₄ -		H	H	SnCl ₄	96	120.9	2245
					BF ₃ ·Et ₂ O	84		
					AlCl ₃	74		
(2b)	-[CH ₂] ₅ -		H	H	SnCl ₄	93	121.5	2250
(2c)	-[CH ₂] ₆ -		H	H	SnCl ₄	95	122.0	2245
(2d)	Pr ⁿ	H	H	Pr ⁿ	SnCl ₄	94	120.3	2240
(2e)	Pr ⁿ	Pr ⁿ	H	H	SnCl ₄	90	120.4	2240
(2f)	H	Et	H	Bu ⁿ	SnCl ₄	91 ^e	122.3 (major) ^f	2240
							117.2 (minor)	
							123.6 (major) ^f	
(2g)	-[CH ₂] ₄ -		Me	H	SnCl ₄	87 ^e	120.1 (minor)	2230
(2h)	H	C ₆ H ₁₃	H	H	SnCl ₄	83 ^e	121.2 (minor) ^f	2250
							118.0 (major)	

^a All reactions were performed at 15 °C under dry argon in dichloromethane (distilled from calcium hydride under argon) using an equimolar ratio of (1), (2), and catalyst. ^b Isolated yield after column chromatography on silica gel. ^c In CDCl₃ with tetramethylsilane as an internal standard. ^d Liquid film. ^e Combined yield of inseparable regioisomer mixture. ^f See text for isomer ratio.

The results for the reactions of other olefins are also included in Table 1. The yields were uniformly excellent when SnCl₄ was used as the catalyst. Each cyclic olefin [cyclopentene (2b) and cycloheptene (2c)] gave a single stereoisomer within the limits of ¹³C n.m.r. detection, suggesting again that the reactions are stereoselective. That the reaction is stereospecific was clearly demonstrated by using *trans*- and *cis*-oct-4-enes [(2d) and (2e)]; the respective phenylseleno carbonitriles [(3d) and (3e)], each obtained as a single stereoisomer, were shown by ¹³C n.m.r. to be different from each other. As expected, 2-ethylhex-1-ene (2f) afforded a mixture of two regioisomers, (3e) (the tertiary carbonitrile) and (3e') (the primary carbonitrile), in the ratio 86:14 (¹H n.m.r.). The preponderant formation of the Markovnikov product (3e) is interesting in that the reaction may serve as a useful route to tertiary carbonitriles to which access is difficult. Similarly, other unsymmetrical alkenes [1-methylcyclohex-1-ene (2g) and oct-1-ene (2h)] gave regioisomer mixtures. In the case of (2g), the major isomer (83%) was the tertiary carbonitrile (Markovnikov product), whereas (2h) afforded the primary carbonitrile (anti-Markovnikov product) as the major regioisomer (85%). The regiochemical assignments of these products were based on ¹H and ¹³C n.m.r. spectra (primary CN; δ 117–118, secondary and tertiary CN; δ 120–123 p.p.m.).

These results indicate that cyanoselenenylation of olefins with phenyl selenocyanate (1) would probably proceed by a mechanism involving completely stereospecific anti-addition across the carbon-carbon double bond. The reactions may be considered as a selenium version of hydrocyanation of an

unactivated carbon-carbon double bond, which is relatively rare and in general requires sensitive catalysts.⁶ The products (3) can be readily converted into α,β-unsaturated carbonitriles by selenoxide *syn*-elimination. For example, (3a) afforded cyclohex-1-enecarbonitrile (4) in 93% isolated yield upon oxidation with 30% aqueous hydrogen peroxide in dichloromethane (room temp., 30 min).

We thank the Ministry of Education (Japanese Government) for the purchase of a JEOL FX-90Q spectrometer which was used in this work.

Received, 27th April 1982; Com. 474

References

- (a) H. J. Reich, *Acc. Chem. Res.*, 1979, **12**, 22; (b) D. L. J. Clive, *Tetrahedron*, 1978, **34**, 1049; (c) K. C. Nicolaou, *Tetrahedron*, 1981, **37**, 4097.
- (a) O. Behaghel and H. Seibert, *Ber.*, 1932, **65**, 812; (b) S. Tomoda, Y. Takeuchi, and Y. Nomura, *Chem. Lett.*, 1981, 1069.
- S. Tomoda, Y. Takeuchi, and Y. Nomura, *Tetrahedron Lett.*, 1982, **23**, 1361.
- Organoselenium species have been activated by Lewis acids; W. P. Jackson, S. V. Ley, and J. A. Morton, (a) *Tetrahedron Lett.*, 1981, **22**, 2601; (b) *J. Chem. Soc., Chem. Commun.*, 1980, 1028.
- (a) A. Toshimitsu, T. Aoai, S. Uemura, and M. Okano, *J. Org. Chem.*, 1981, **46**, 3021; (b) S. Tomoda, Y. Takeuchi, and Y. Nomura, *Chem. Lett.*, 1982, 253.
- Recent examples; (a) P. S. Elmes and W. R. Jackson, *J. Am. Chem. Soc.*, 1979, **101**, 6128; (b) J. Backvall and O. S. Andell, *J. Chem. Soc., Chem. Commun.*, 1981, 1098.