Synthesis of 1-Phenylselenobuta-1,3-diene and its Methyl-substituted Homologues *via* Oxyselenation of Conjugated Dienes

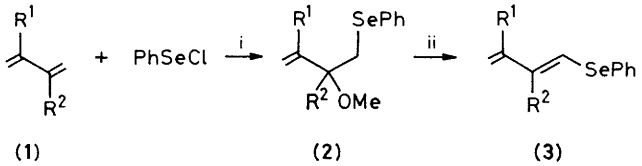
Akio Toshimitsu,* Sakae Uemura, and Masaya Okano

Institute for Chemical Research, Kyoto University, Uji, Kyoto 611, Japan

Methoxyselenation of conjugated dienes followed by treatment with lithium di-isopropylamide constitutes a convenient method for the preparation of 1-phenylselenobuta-1,3-diene and its methyl-substituted homologues.

Phenylselenobutadienes are promising synthetic intermediates owing to their useful vinylselenide structure[1] as well as the expected reactivity as dienes in, for instance, the Diels–Alder reaction. Their preparation, however, has so far been limited only to highly functionalized dienes.[2] We report here a convenient method for the preparation of a simple 1-phenylselenobuta-1,3-diene and its methyl-substituted homologues *via* the methoxyselenation of conjugated dienes followed by the elimination of methanol.

By treating the conjugated dienes (**1**) with benzeneselenenyl chloride in methanol as solvent, Markownikoff-type 1,2-addition products (**2**) were formed in excellent yields.† In the case where isoprene was used as the conjugated diene, a mixture of regioisomers, (**2b**) and (**2c**), was formed. The main product was (**2b**) in the reaction at room temperature for 2 h (expt. 2), while (**2c**) was found to be the major product when



(1) (2) (3)

a; $R^1 = R^2 = H$
b; $R^1 = Me$, $R^2 = H$
c; $R^1 = H$, $R^2 = Me$
d; $R^1 = R^2 = Me$

Scheme 1. *Reagents:* i, MeOH; ii, $LiNPr^i_2$, THF.

triethylamine was added to the reaction mixture (expt. 3). Compound (**2b**) can be separated from (**2c**) quite easily by column chromatography. Methoxyselenation of 2,3-dimethylbuta-1,3-diene was also carried out in the presence of triethylamine to avoid isomerization to the 1,4-addition products. Typical results are summarized in Table 1.

Elimination of methanol from (**2**) was carried out by treatment with lithium di-isopropylamide in tetrahydrofuran (THF) under a nitrogen atmosphere. As shown in Table 2, 1-phenylseleno-1,3-butadiene and its methyl-substituted homologues (**3**) were isolated in almost quantitative yields.† Although (**3**) is somewhat unstable and decomposes during purification by methods such as distillation or column chromatography, spectroscopically pure (**3**) was obtained by

Table 1. Methoxyselenation of conjugated dienes.[a]

Expt.	(1) R^1	(1) R^2	Temp./°C	Time/h	Additive; 5 mmol	Product(s); yield,[b] %
1	H	H[c]	25	3	——	(**2a**); 90
2	Me	H	25	2	——	(**2b**); 83, (**2c**); 3[d]
3	Me	H	25	24	Et_3N	(**2b**); 22, (**2c**); 61[d]
4	Me	Me	0	2	Et_3N	(**2d**); 98

[a] Carried out using (**1**) (15 mmol) and PhSeCl (5 mmol) in methanol (25 ml). [b] Isolated yield after column chromatography. [c] Carried out in a pressure bottle using *ca.* 25 mmol of (**1**). [d] In addition a mixture of 1,4-addition products were formed; 10% in expt. 2 and 1% in expt. 3.

Table 2. Reaction conditions for the preparation of (**3**).[a]

Expt.	(2)	$LiNPr^i_2$/mmol	Temp./°C	Time/h	Product; yield,[b] %
5	(**2a**)	6	—78	1	(**3a**); 100
6	(**2b**)	5	—78	1	(**3b**); 96
7	(**2c**)	8	0	0.8	(**3c**); 100
8	(**2d**)	8	0	2	(**3d**); 88

[a] Carried out using (**2**) (4 mmol) in tetrahydrofuran (20 ml) under nitrogen atmosphere. [b] Isolated yield.

† Satisfactory i.r., ^1H n.m.r., and ^{13}C n.m.r. data as well as mass spectral data were obtained for all new compounds. Some typical n.m.r. spectral data are as follows (phenyl signals are omitted). (**2b**) ($CDCl_3$, 100 MHz ^1H n.m.r.); δ 1.68 (3H, t, *J* 1 Hz), 3.01 (1H, dd, *J* 12, 6 Hz), 3.19 (1H, dd, *J* 12, 7.5 Hz), 3.24 (3H, s), 3.79 (1H, dd, *J* 7.5, 6 Hz), and 5.02 (2H, br.s). (**2c**) ($CDCl_3$, 100 MHz ^1H n.m.r.); δ 1.40 (3H, s), 3.12 (1H, d, *J* 12 Hz), 3.19 (3H, s), 3.24 (1H, d, *J* 12 Hz), 5.24 (1H, dd, *J* 18, 1.5 Hz), 5.26 (1H, dd, *J* 10, 1.5 Hz), and 5.89 (1H, dd, *J* 18, 10 Hz). (**3b**) ($CDCl_3$, ^{13}C n.m.r.); δ 18.3 (q), 116.0 (t), 119.4 (d), 137.9 (d), and 141.2 p.p.m. (s). (**3c**) ($CDCl_3$, ^{13}C n.m.r.); δ 15.2 (q), 111.3(t), 124.5 (d), 137.5 (s), and 138.7 p.p.m. (d).

evaporation of solvent after the usual work-up procedure. ^{13}C N.m.r. spectra of compounds (**3**) indicate that each of (**3a—d**) consists of one stereoisomer, presumably with the phenylseleno-group in the *trans*-position to a bulky vinyl substituent. When R^2 is a methyl group, elimination of methanol is somewhat slower and the use of excess of lithium di-isopropylamide at higher temperatures is required to complete the elimination without side-reaction (expts. 7 and 8). It is noteworthy that the selective formation of either (**3b**) or (**3c**), both of which possess a valuable isoprene unit, was realized by this two step procedure.

Received, 27th May 1982: Com. 608

References

1 W. Dumont, M. Sevrin, and A. Krief, *Angew. Chem., Int. Ed. Engl.*, 1977, **16**, 541; M. Sevrin, W. Dumont, and A. Krief, *Tetrahedron Lett.*, 1977, 3835; W. Dumont, M. Sevrin, and A. Krief, *ibid.*, 1978, 183; M. Sevrin, J. N. Denis, and A. Krief, *Angew. Chem., Int. Ed. Engl.*, 1978, **17**, 526; S. Raucher and G. A. Koolpe, *J. Org. Chem.*, 1978, **43**, 3794, 4252; A. E. Feiring, *ibid.*, 1980, **45**, 1958, 1962; M. Shimizu and I. Kuwajima, *ibid.*, 1980, **45**, 2921, 4063; M. Shimizu, R. Ando, and I. Kuwajima, *ibid.*, 1981, **46**, 5246.

2 S. Danishefsky, C. F. Yan, and P. M. McCurry, Jr., *J. Org. Chem.*, 1977, **42**, 1819; S. Danishefsky, C. F. Yan, R. K. Singh, R. B. Gammill, P. M. McCurry, Jr., N. Fritsch, and J. Clardy, *J. Am. Chem. Soc.*, 1979, **101**, 7001; H. J. Reich, J. J. Rusek, and R. E. Olson, *ibid.*, 1979, **101**, 2225.