Acknowledgment. We wish to acknowledge the advice and encouragement of Professor H. P. Broquist, the assistance of Mr. James S. Hubbard in obtaining mass spectra, and financial support for this project by the U.S. Public Health Service [ES-00267 (Vanderbilt University Center in Environmental Toxicology) and AM-14338].

Registry No.—**1**, 15862-72-3; **2**, 67425-79-0; **3**, 67425-80-3; **5**, 67425-81-4; **7**, 67425-82-5; **8**, 65172-11-4; **9**, 65171-90-6; ethyl propiolate, 623-47-2; proline ethyl ester, 5817-26-5; methylaminoacetic acid ethyl ester, 13200-60-7.

References and Notes

(1) For a review on this alkaloid, see F. P. Guengerich and H. P. Broquist in "A Survey of Contemporary Bioorganic Chemistry", Vol II, E. E. van Tamelen, Ed., Academic Press, New York, N.Y., 1976.

(2) E. Winterfeldt and H. J. Dillinger, *Chem. Ber.*, **99**, 1558 (1966). These workers converted the Michael adduct into a pyrrole derivative by treatment with potassium metal in toluene; the Dieckmann ring closure involved nucleophilic attack on the maleate terminal carbonyl group rather than on the carbonyl group of the acetate fragment. Winterfeldt and Dillinger also achieved a one-step condensation–cyclization involving the acetate carbonyl group by employing methyl diethylaminoacetate with dimethyl acetylenedicarboxylate.

(3) For a review of related reactions of acetylene compounds with amino acids, see M. V. George, S. K. Khetan, and R. K. Gupta, *Adv. Heterocycl. Chem.*, **19**, 279 (1976).

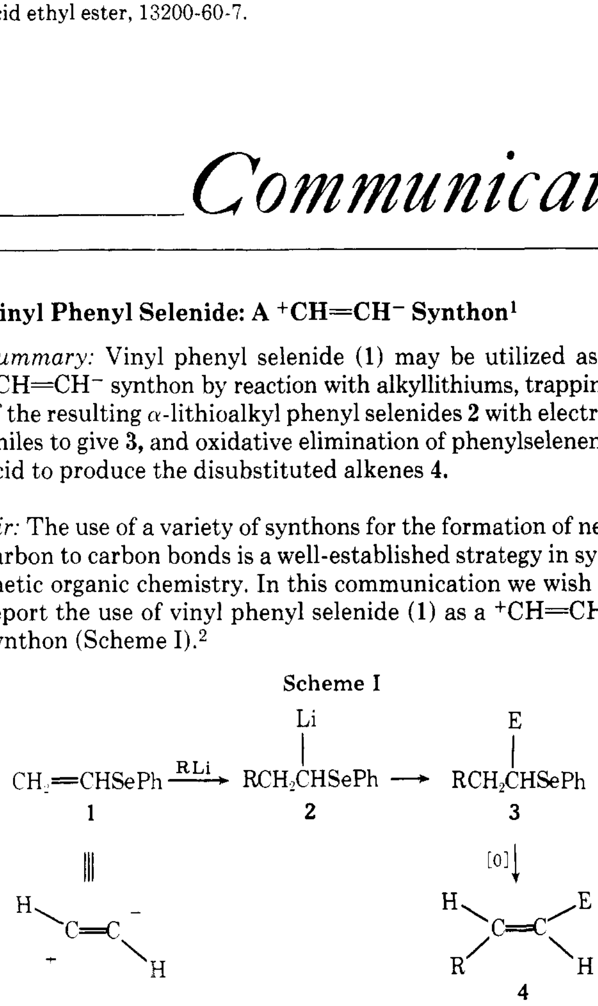
Communications

Vinyl Phenyl Selenide: A $^+CH{=}CH^-$ Synthon[1]

Summary: Vinyl phenyl selenide (**1**) may be utilized as a $^+CH{=}CH^-$ synthon by reaction with alkyllithiums, trapping of the resulting α-lithioalkyl phenyl selenides **2** with electrophiles to give **3**, and oxidative elimination of phenylselenenic acid to produce the disubstituted alkenes **4**.

Sir: The use of a variety of synthons for the formation of new carbon to carbon bonds is a well-established strategy in synthetic organic chemistry. In this communication we wish to report the use of vinyl phenyl selenide (**1**) as a $^+CH{=}CH^-$ synthon (Scheme I).[2]

Scheme I



The addition of alkyllithiums to a number of vinyl derivatives of second-row elements in their lower oxidation states has been reported.[3] We felt that such additions to vinyl phenyl selenides would be particularly useful for the following reasons: (1) the ability of a phenylseleno group to stabilize an adjacent carbanion and the reaction of these carbanions with a variety of electrophiles has been demonstrated;[4] (2) subsequent to performing its function, the phenylseleno group may be easily removed via oxidative elimination of phenylselenenic acid to generate alkenes, often regio- and stereospecifically;[5] and (3) the requisite vinyl phenyl selenides are readily available.[6]

Although vinyl phenyl selenide (**1**) is unreactive toward both n-Bu_2CuLi and n-BuMgBr, alkyllithiums readily add to **1**[7] in dimethoxymethane or diethyl ether at 0 °C to give the α-lithioalkyl phenyl selenides **2**, which may be trapped by electrophiles to give the substituted alkyl phenyl selenides **3**; oxidative elimination of phenylselenenic acid for instances in which the regiospecificity is unambiguous (e.g., E = $>C{=}O$ or $>COH$) leads to the formation of the E-disubstituted alkenes **4** in good overall yield (Table I).[8]

Since the reaction of alkyllithiums with **1** can also lead to α-deprotonation[9] or carbon–selenium bond cleavage,[10] the proper choice of reaction conditions is essential for the success of the desired addition reaction (Scheme II). In particular,

Table I. Alkyllithium Addition–Electrophile Trapping with Vinyl Phenyl Selenide[a]

entry	RLi	electrophile	E	% yield 3	% yield 4
a	n-BuLi	D_2O	D–	97	
b	n-BuLi	CH_3I[b]	CH_3–	95	
c	n-BuLi	n-$C_{10}H_{11}Br$[b]	n-$C_{10}H_{21}$–	80	
d	n-BuLi	PhSeBr	PhSe–	84	*c*
e	n-BuLi	$(CH_3)_3SiCl$	$(CH_3)_3Si$–	90	*d*
f	n-BuLi	PhCHO	PhCH(OH)–	71	75[h]
g	n-BuLi	CH_3COCH_3	$(CH_3)_2C(OH)$–	60	83[h]
h	n-BuLi	$PhCOCH_3$	$PhC(CH_3)(OH)$–	*e*	50[f,h]
i	n-BuLi	PhCN	PhCO–	*e,g*	61[f,h]
j	i-PrLi	D_2O	D–	92	
k	i-PrLi	CH_3COCH_3	$(CH_3)_2C(OH)$–	72	81[h]
l	i-PrLi	$(CH_3)_3SiCl$	$(CH_3)_3Si$–	86	*d*
m	t-BuLi	D_2O	D–	85	

[a] Yields refer to isolated, purified products. See ref 8. All reactions utilize 1.2 equiv of alkyllithium and 1.2–1.5 equiv of electrophile (except D_2O quenches). Reactions with n-BuLi were run in dimethoxymethane; reactions with i-PrLi and t-BuLi were run in diethyl ether. [b] 1 equiv of HMPA was added with the electrophile. [c] Bis(phenylseleno) acetals may be hydrolyzed to the corresponding aldehydes; thus, **1** is also a $^+CH_2CHO$ synthon. [d] Oxidation of (α-trimethylsilyl)alkyl phenyl selenides affords the corresponding aldehydes: K. Sachdev and H. S. Sachdev, *Tetrahedron Lett.*, 4223 (1976). [e] Intermediate not isolated. [f] Overall yield from **1**. [g] Hydrolyzed with 5% HCl (75 °C, 15 min) prior to oxidation–elimination. [h] Only the *E* isomer was produced.

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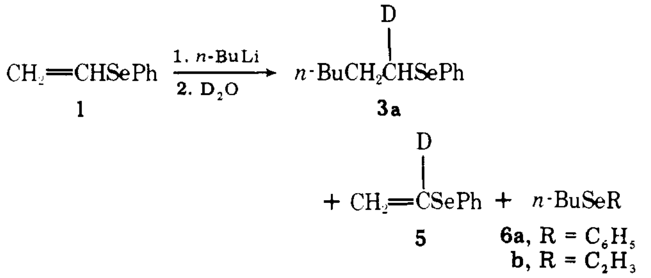
Table II. Solvent–Temperature Effects for the Reaction of *n*-BuLi with 1[a]

solvent	temp, °C	% products[b] 3a	5[c]	6
$(CH_3O)_2CH_2$	0	97	3	0
Et_2O	0	90	10	0
Et_2O	−78	55	15[d]	0
THF	0	70	20	10
THF	−78	5	15	80

[a] All reactions were 0.1 M in 1 and utilized 1.2 equiv of *n*-BuLi; after 1 h the reactions were quenched with excess D_2O. [b] Determined by VPC on 5 ft × 1/4 in. 1.5% OV 101 on 100/120 Chromosorb G column. In all cases, mass balance was >80%. [c] Deuterium incorporation verified by NMR. [d] Amount of 5 estimated by NMR; unreacted 1 accounted for the remainder of the mass.

Scheme II



solvent and temperature effects are crucial, with dimethoxymethane or diethyl ether at 0 °C providing the best results in preliminary studies involving the addition of *n*-BuLi to 1 followed by quenching with D_2O (Table II). Related solvent effects have been previously observed for the reaction of alkyllithiums with alkenes, and, although complex, may be related to the state of aggregation of the alkyllithium reagent.[11]

We are currently investigating the use of vinyl phenyl selenides as synthons in a number of other reactions; these results will be reported in due course.

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(2) (a) E. J. Corey, *Pure Appl. Chem.*, **14**, 19 (1967); (b) D. Lednicer, *Adv. Org. Chem.*, **8**, 179 (1972). (c) For the use of HC≡CH as a $^+CH{=}CH^-$ equivalent via addition of cuprates and trapping by electrophiles see: A. Alexakis, J. Normant, and J. Villieras, *Tetrahedron Lett.*, 3461 (1976). It is noteworthy that this procedure yields (*Z*)-alkenes, thus making it complementary to the selenoxide elimination, which produces (*E*)-alkenes.

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(6) (a) Vinyl phenyl selenide (1) is readily prepared by dehydrohalogenation (1.2 equiv of *t*-BuOK in THF, 25 °C) of 2-chloroethyl phenyl selenide, prepared by reaction of $PhSe^-$ (PhSeSePh, $NaBH_4$, EtOH) with excess 1,2-dichloroethane (50 equiv), in 95% overall yield from PhSeSePh. (b) Substituted vinyl phenyl selenides are available from the corresponding alkenes: S. Raucher, *J. Org. Chem.*, **42**, 2950 (1977).

(7) (a) Reaction of vinyl phenyl selenoxide with *n*-BuLi or *n*-Bu_2CuLi led to products resulting from carbon–selenium bond cleavage. (b) We have been unable to effect addition of methyllithium to 1.

(8) (a) All new compounds were fully characterized by spectroscopic methods. Yields are given for chromatographically pure, isolated products. (b) A typical experimental procedure for the preparation of (*E*)-2-methyl-3-octen-2-ol (**4g**) follows. A solution of vinyl phenyl selenide (**1**) (305 mg, 1.67 mmol) in freshly dried (CaH_2) dimethoxymethane (1.5 mL) was added over 10 min to a solution of *n*-BuLi (2.4 M in hexane, 0.83 mL, 2.0 mmol) in dimethoxymethane (5.0 mL) at 0 °C under an atmosphere of argon. The clear solution was stirred at 0 °C for 1 h, cooled to −78 °C, and a solution of acetone (145 mg, 2.5 mmol) in THF (2.0 mL) was added over 10 s, and stirring was continued at −78 °C for 1 h. The reaction mixture was quenched with aqueous NH_4Cl, extracted with ether, and dried ($MgSO_4$), and the solvents were removed in vacuo to give crude 2-methyl-3-phenylseleno-2-octanol (**3g**), which was dissolved in CH_2Cl_2 (15 mL), cooled to −78 °C, and ozonized[5e] for 5 min. Diisopropylamine (1 mL)[4g] and CCl_4 (25 mL) were added, the mixture was refluxed for 30 min, the solvents were removed in vacuo, and the residue was purified on silica gel (20 g) with hexane–ether to give (*E*)-2-methyl-3-octen-2-ol as a clear liquid (117 mg, 50% overall from **1**): ^1H NMR (CCl_4) δ 0.70–2.20 (m) and 1.25 (s) [total 15 H], 2.75 (bs, 1 H, OH), 5.58 (m, 2 H). (c) Additional ^1H NMR data (CCl_4): **3a** δ 0.70–1.90 (m, 12 H), 2.85 (t, J = 6 Hz, 1 H), 7.10–7.60 (m, 5 H); **3b** δ 0.70–1.90 (m) and 1.34 (d, J = 7 Hz) [total 14 H], 3.20 (m, 1 H), 7.05–7.80 (m, 5 H); **3d** δ 0.70–2.10 (m, 11 H), 4.41 (t, J = 6 Hz, 1 H, $-C\mathbf{H}(SePh)_2$), 7.10–7.70 (m, 10 H); **3e** δ 0.08 (s, 9 H), 0.67–1.75 (m, 11 H), 2.30 (t, J = 6 Hz, 1 H, $-C\mathbf{H}(SePh)SiMe_3$), 7.00–7.60 (m, 5 H); **3f** δ 0.68–1.80 (m, 11 H), 3.30 (m) and 3.51 (bs) [total 2 H], 4.51 (d, J = 8 Hz, 1 H, $PhC\mathbf{H}(OH)CH<$), 7.15–7.70 (m, 10 H); **3g** δ 0.70–2.00 (m), 1.28 (s) and 1.44 (s) [total 17 H], 2.80 (bs, 1 H), 3.18 (m, 1 H), 7.20–7.80 (m, 5 H); **3j** δ 0.92 (d, J = 7 Hz, 6 H), 1.12–1.98 (m, 4 H), 2.87 (t, J = 7 Hz, 1 H), 7.10–7.62 (m, 5 H); **3k** δ 0.75 (d, J = 7 Hz), 0.97 (d, J = 7 Hz), 1.21 (s), 1.33 (s), and 1.40–2.00 (m) [total 14 H], 2.72 (bs, 1 H), 3.15 (m, 1 H), 7.06–7.74 (m, 5 H); **3m** δ 0.88 (s, 9 H), 1.50 (m, 2 H), 2.83 (t, J = 9 Hz), 7.10–7.58 (m, 5 H); **4f** δ 0.70–1.65 (m, 7 H), 2.06 (m, 2 H), 2.88 (bs, 1 H), 5.04 (m, 1 H), 5.61 (m, 2 H), 7.20–7.42 (m, 5 H); **4h** δ 0.70–1.65 (m) and 1.57 (s) [total 9 H], 2.00 (m, 2 H), 5.47 (d of t, J = 14 and 5 Hz), 5.68 (d, J = 14 Hz) [total 2 H], 7.16–7.60 (m, 5 H); **4i** δ 0.70–1.80 (m, 7 H), 2.38 (m, 2 H), 6.95 (m, 2 H), 7.32–8.10 (m, 5 H); **4j** δ 0.98 (d, J = 7 Hz, 6 H), 1.26 (s, 6 H), 1.91 (m, 1 H), 2.42 (bs, 1 H), 5.53 (m, 2 H).

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Template Synthesis of Macromolecules. Selective Functionalization of an Organic Polymer

Summary: Hydrolysis of a copolymer of divinylbenzene and bis(vinylbenzyl) *trans*-1,2-cyclobutanedicarboxylate liberates polymer-bound benzyl alcohol groups; rebinding studies and chemical transformations of the benzyl alcohol groups suggest that the functional groups are capable of retaining some stereochemical information originally present in the cyclobutane diester.

Sir: The ability to selectively introduce organic functionality in fixed geometrical relationships has remained a longstanding challenge to chemists. A variety of ingenious approaches have been employed to accomplish this goal.[1] A technique recently developed by Wulff and co-workers[2] strikes us as having the

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