53188-81-1; (11), $R^4 = C_6H_5$, $R^5 = H$, 20157-19-1; (12), $R^4 = R^5 = C_6H_5$, 1454-57-5

[1] Unstabilized selenonium ylides can be generated by reaction of suitable bases with selenonium salts: *W. Dumont, P. Bayet,* and *A. Krief,* Angew. Chem. 86, 308 (1974); Angew. Chem. internat. Edit. 13, 274 (1974).

[2] Similar cleavage of some selenides has been described: a) H. Gilman and R. L. Bebb, J. Amer. Chem. Soc. 61, 1110 (1939); b) H. Gilman and F. J. Webb, J. Amer. Chem. Soc. 71, 4064 (1949); c) D. Seebach and N. Peleties, Angew. Chem. 81, 465 (1969); Angew. Chem. internat. Edit. 8, 450 (1969); d) D. Seebach and N. Peleties, Chem. Ber. 105, 511 (1972). However, no systematic study was performed.

[3] Reaction conditions: a) To a suspension of 6 mmol of (1) in THF (10 ml) was added (at -78 °C, under N₂) 5.5 mmol of *n*-butyllithium in hexane (2.75 ml). After 10 min, the carbonyl compound (5 mmol in 5 ml THF) was introduced and the mixture was allowed to react for 2 h at -78 °C and 1 h at 20 °C. b) To a solution of 6 mmol of (6) in THF (10 ml) was added (at 0 °C. under N₂) 5.5 mmol of *n*-butyllithium in hexane (2.75 ml). After 15 min at 0 °C and 30 min at 20 °C, the carbonyl compound (5 mmol in 5 ml THF) was introduced and the mixture was allowed to react for 2 h at -32 °C.

[4] See a) G. Wittig and H. Fritz, Liebigs Ann. Chem. 577, 41 (1962); b) D. Hellwinkel and G. Farbach, ibid. 715, 68 (1968).

[5] D. Seebach [2c, 2d] reported one example of this type: cleavage of bis(phenylseleno)methane with n-butyllithium to give phenylselenomethyllithium which was trapped by reaction with benzophenone.

[6] K. B. Sharpless and R. F. Lauer, J. Amer. Chem. Soc. 95, 2697 (1973). [7] Reaction conditions: To a solution of sclenoketal (14) (5.2 mmol) in THF (10 ml) was added a solution of n-butyllithium (5.2 mmol) at -78 °C under N₂. After stirring for a further 1.5 h (not optimized), (3) (5 mmol) in THF (5 ml) was slowly introduced. The mixture was allowed to react for 2 h at -78 °C and 2 h (15 h with acetophenone) at 25°C, hydrolyzed and worked up in the usual manner.

Secondary and Tertiary Phenylthio- and Phenylselenoalkyllithium Compounds as Novel Reagents for the Formation of C—C Bonds^[***]

By Dieter Seebach and Albert K. Beck^[*]

Because of its pronounced nucleophilic character, phenylthiomethyllithium (2), R = R' = H, which is readily accessible by metalation of thioanisol^[1], has acquired considerable preparative significance as a CH₂ synthon in methylenations of car-



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bonyl compounds to give olefins^[2a] and epoxides^[2b] and for the homologization of primary halides^[2c]. However, a wide range of variation of the transfer group seemed to be precluded^[2b] by the tendency of alkyl aryl sulfides containing higher alkyl groups to undergo *o*-metalation on reaction with *n*-butyllithium. (Ring metalation is favored thermodynamically by a factor of at least $50^{[3]}$.)

We have now found C₆H₅Se/Li exchange^[4], which is comparable with Br/Li exchange, to offer a kinetically controlled method for the preparation of secondary and tertiary phenylseleno- (1) and phenylthio-alkyllithium compounds (2). The selenoacetals (3) obtained from aldehydes or ketones or by alkylation of (1), $R = SeC_6H_5$, $R' = H^{[4b]}$ are converted into the selenium-substituted derivatives (1) within 15 min on treatment with *n*- or *tert*-butyllithium in THF at -80°C. The products can be transformed by thiolation into the S, Se acetals (4) which yield the sulfur-substituted derivatives (2) on renewed transmetalation. Reaction of the organolithium compounds (1) or (2) with electrophiles furnishes the products (5) and (6) respectively (Table 1).

As can be seen from Scheme 1, the phenylseleno- (7) and phenylthio-alkyl alcohols (8) prepared with aldehydes and ketones as electrophiles are actually formed by coupling of the carbonyl C atoms of *two* aldehydes or ketones. The selenium derivatives (7) can be oxidized^[5] to yield allyl alcohols (9) or (10), e.g. (9a) from cyclohexanone and hexanal (overall yield 50%) or (10a) from cyclohexanone and acetone (overall yield 65%). Hence compounds of type (1) can be regarded as masked *vinyllithium compounds*.



Scheme 1. Transformations possible with the organolithium compounds (1) and (2) and ketones and aldehydes as electrophiles.

The olefins (11) and epoxides (12) should likewise be accessible from the selenium- $(7)^{[6]}$ or sulfur-containing alcohols $(8)^{[2a, 2b]}$ by known methods.

Table 1. Starting materials, yields, and physical data of compounds of types (3)---(8), (9a), and (10a).

Cpd.	Prepared from	Yield $\begin{bmatrix} 0 \\ 0 \end{bmatrix}$	NMR characterization (8 [ppm] in CCl ₄ , J [Hz])
(3), $R = CH_3$, $R' = H$	(1), $R = SeC_{6}H_{5}$, $R' = H_{1} + CH_{3}I$	95 [a]	see [4b]
(3), $R = n - C_{10} H_{21}$, $R' = H$	(1), $R = SeC_6H_5$, $R' = H_1 + n - C_{10}H_{21}Br$	76 [b]	α -SeCH: 4.40 (t, 6.0)
$(3), R = R' = CH_3$	acetone + $2C_{6}H_{5}SeH$	80 [c]	see [4b]
(3), $R - R' = -(CH_2)_5$	cyclohexanone + $2 C_6 H_5 SeH$	95 [d]	
$(4), R = CH_3, R' = H$	(1), $R = CH_3$, $R' = H_5 + (C_6H_5S)_2$	60 [c]	CH ₃ : 1.67 (d, 7.0); CH: 4.48 (t, 7.0)
$(4), R = R' = CH_3$	(1), $R = R' = CH_3$, + $(C_6H_5S)_2$	70 [ſ]	CH ₃ : 1.57 (s)
$(5), R = CH_3, R' = H, E = D$	(1), $R = CH_3$, $R' = H_3 + D_2O$	>98	CH ₃ : 1.35 (broadened by D-coupling d, 7.0); α -Se—CHD: 2.72 (broadened by D-coupling q, 7.0)
(7), $R = CH_3$, $R' = H$, $R'' - R''' = -(CH_2)_5 -$	(1), $R = CH_3$, $R' = H_1 + cyclohexanone$	72 [g]	CH ₃ : 1.45 (d, 7.5); α-SeCH: 3.24 (q, 7.5)
(7), $\mathbf{R} = \mathbf{CH}_3$, $\mathbf{R}' = \mathbf{H}$, $\mathbf{R}'' - \mathbf{R}''' = -(\mathbf{CH}_2)_{7} $	(1), $R = CH_3$, $R' = H_3 + cyclooctanone$	65 [g]	CH ₃ : 1.50 (d, 7.0); α-SeCH: 3.40 (q, 7.0)
(5), $R = n - C_{10}H_{21}$, $R' = H$, $E = H$	(1), $R = n - C_{10} H_{21}$, $R' = H_1 + H_2 O_1$	> 95	α -SeCH ₂ : 2.83 (t, 6.8)
(5), $R = n - C_{10}H_{21}$, $R' = H$, $E = D$	(1), $R = n - C_{10} H_{21}$, $R' = H_1 + D_2 O_1$	>95	α-Se-CHD: 2.84 (broadened by D-coupling t, 6.8)
$(5), R = R' = CH_3, E = D$	$(1), R = R' = CH_3, + D_2O$	> 98	CD(CH ₃) ₂ : 1.37 (broadened by D-coupling s)
(7), $R = R' = CH_3$, $R'' - R''' = -(CH_2)_5$	(1), $R = R' = CH_3$, + cyclohexanone	85 [g]	CH ₃ : 1.35 (s)
(7), $R - R' = -(CH_2)_5 - R'' = n - C_5 H_{11}, R''' = H_{11}$	(1), $R - R' = -(CH_2)_5 - + hexanal$	80 [g]	α -OCH: 3.15 (m); terminal CH ₃ : 0.88 (deg. t)
(6), $R = CH_3$, $R' = H$, $E = D$	(2), $R = CH_{3}$, $R' = H_{2} + D_{2}O$	> 98	x-SCHD: 1.26 (broadened by D-coupling d, 7.0)
(8), $R = CH_3$, $R' = H$, $R'' = R''' = C_6H_5$	(2), $R = CH_3$, $R' = H_3$, + benzophenone	80	CH ₃ : 1.17 (d, 7.0); α-S=CH: 4.27 (q, 7.0)
(6), $R = R' = E = CH_3$	(2), $R = R' = CH_3$, + CH_3I	40 [h]	$C(CH_3)_3$: 1.58 (s)
(8), $\mathbf{R} = \mathbf{R}' = \mathbf{CH}_3$, $\mathbf{R}'' - \mathbf{R}''' = -(\mathbf{CH}_2)_5 - \mathbf{CH}_2$	(2), $R = R' = CH_3$, + cyclohexanone	95 [g]	CH ₃ : 1.18 (s)
(9a)	(7), $R - R' = -(CH_2)_{5} - $,	65	vinylic H: 5.6 (m)
	$R'' = n - C_5 H_{11}, R''' = H_1 + H_2 O_2$ in T	HF	
(10a)	(7), $R = R' = CH_3$, $R'' - R''' = -(CH_2)_5 -$, + H_2O_2 in THF	95 [i]	CH ₃ : 1.75 (broadened by allyl-coupling s); vinylic H <i>cis</i> to CH ₃ : 4.70 (m); vinylic H <i>trans</i> to CH ₃ : 4.92 (m)

[a] B.p. 140-146°C/0.1 torr. [b] B.p. 130°C/0.02 torr. [c] B.p. 141-144°C/0.08 torr.

[d] M.p. 76.5--77.5°C. [e] B.p. 109°C/0.02 torr. [f] B.p. 130°C/0.3 torr.

[g] The alcohols were separated from $C_6H_5SeC_4H_9$ by chromatographic filtration over silica gel or by preparative TLC and isolated pure as oils.

[h] Separated by gas chromatography. [i] $n_D^{23} = 1.4822$ ([7]: $n_D^{26} = 1.4800$).

The modes of preparation, yields, and physical and NMR data of the compounds of types (3)—(8), (9a), and (10a)obtained are listed in Table 1.

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CAS Registry numbers: (1), $R = SeC_6H_5$, R' = H, 53198-49-5; (1), $R = CH_3$, $\begin{array}{l} \mathsf{R}' = \mathsf{H}, \ 53198{\text{-}}50{\text{-}}8; \ (1), \ \mathsf{R} = \mathsf{R}' = \mathsf{CH}_3, \ 53230{\text{-}}01{\text{-}}6; \ (1), \ \mathsf{R} = n{\text{-}}\mathbf{C}_{10}\mathsf{H}_{21}, \ \mathsf{R}' = \mathsf{H}, \\ 53198{\text{-}}51{\text{-}}9; \ (1), \ \mathsf{R} = -\mathsf{R}' = (\mathsf{CH}_2)_5, \ 53198{\text{-}}52{\text{-}}0; \ (2), \ \mathsf{R} = \mathsf{CH}_3, \ \mathsf{R}' = \mathsf{H}, \\ \end{array}$ 53198-53-1; (2), $R = R' = CH_3$, 53198-54-2; (3), $R = CH_3$, R' = H, 26822-85-5; (3), $R = n-C_{10}H_{21}$, R' = H, 53198-55-3; (3), $R = R' = CH_3$, 35446-87-8; (3), $R-R' = (CH_2)_5$, 53198-56-4; (4), $R = CH_3$, R' = H, 53198-57-5; (4), $R = R' = CH_3$, 53198-58-6; (5), $R = CH_3$, $\ddot{R}' = H$, $E = {}^{2}H$, 53198-59-7; (5), $R = n - C_{10}H_{21}$, R' = H, E = H, 53198-60-0; (5), $R = R' = CH_3$, $E = {}^{2}H$, 53198-63-3; (5), $R = n - C_{10}H_{21}$, R' = H, $E = {}^{2}H$. 53198-61-1: (6). $R = CH_3$, R' = H, $E = {}^{2}H$, 53198-62-2; (6), $R = R' = E = CH_3$, 3019-19-0; (7), $\mathbf{R} = \mathbf{CH}_3$, $\mathbf{R}' = \mathbf{H}$, $\mathbf{R}'' = \mathbf{R}''' = (\mathbf{CH}_2)_5$, 53198-64-4; (7), $\mathbf{R} = \mathbf{CH}_3$, $\mathbf{R}' = \mathbf{H}$. $K'' = K'' = (CH_2)_5, S198.65-5; (7), R = R' = (CH_2)_5, S7.86-67, (7), R = CH_3, R'' = H.$ $S3198.66-6; (7), R = R' = CH_3, R'' = R'' = (CH_2)_5, S3188-73-1; (8),$ $R = CH_3, R' = H, R'' = R''' = C_6H_5, 53198-67-7; (8), R = R' = CH_3,$ $R'' - R''' = (CH_2)_5, 53198-68-8; (9a), 53198-69-9; (10a), 3908-31-4;$ CH₃I, 74-88-4; n-C₁₀H₂₁Br, 112-29-8; C₆H₅SeH, 645-96-5; (C₆H₅S)₂ 882-33-7; ²H,O, 7789-20-0; H,O₂, 7722-84-1; Acetone, 67-64-1; Cyclohexanone, 108-94-1; Cyclooctanone, 502-49-8; Hexanal, 66-25-1; Benzophenone, 119-61-9

Chem. internat. Edit. 13, 274 (1974).

[7] C. R. Johnson, C. J. Cheer, and D. J. Goldsmith, J. Org. Chem. 24, 3320 (1964).

Cyclohepta [cd]phenalen-6-one^[1]

By Ichiro Murata, Kagetoshi Yamamoto, and Yutaka Kayane^[*] In connection with current interest in the peripheral conjugation in peri-condensed polyarenes, we have recently reported the synthesis and properties of the phenalenones (1)— $(3)^{[2-4]}$. We have proposed that compounds (1) and (2) can be regarded as perturbed [13]-annulenones and compound (3) as a perturbed [15]-annulenone. In this communication we report the synthesis and properties of a further example of this type of compound, a novel tropone derivative, cyclohepta[cd] phenalen-6-one (9).



Reformatsky reaction of dihydrophenalenone $(4)^{[5]}$ with methyl 4-bromocrotonate afforded the hydroxy ester, which, on hydrogenation with palladium hydroxide on charcoal followed by hydrolysis with potassium hydroxide in ethanol gave the carboxylic acid $(5)^{161}$, m.p. = 90°C, in 48% yield [referred to (4)]. Cyclization of (5) with polyphosphoric acid (PPA) at 90°C for 1 h afforded the tetracyclic ketone $(6)^{[6]}$ in 75% yield : m.p. = 97.5–98 °C; IR (KBr): 1665 cm⁻¹; ¹H-NMR (CDCl₃): $\delta = 1.6$ —2.2 (m, 6H), 2.5—2.7 (m, 2H), 2.9-3.5 (m, 3H) and 7.0-7.7 (m, 5H). The ketone (6) was converted by treatment with bromine in dry carbon tetrachloride into the α, α -dibromoketone (7) in quantitative yield: viscous oil; IR (neat): 1695 cm^{-1} ; ¹H-NMR: $\delta = 1.5 - 2.7$ (m,

^[1] E. J. Corey and D. Seebach, J. Org. Chem. 31, 4097 (1966).

^[2] a) R. L. Sowerby and R. M. Coates, J. Amer. Chem. Soc. 94 4758 (1972); I. Kuwajima, S. Sato, and Y. Kurata, Tetrahedron Lett. 1972, 737; b) J. R. Shanklin, C. R. Johnson, J. Ollinger, and R. M. Coates, J. Amer. Chem. Soc. 95, 3429 (1973); c) E. J. Corey and M. Jautelat, Tetrahedron Lett. 1968. 5787.

^[3] D. A. Shirley and B. J. Reeves, J. Organometal. Chem. 16, 1 (1969). [4] a) H. Gilman and R. L. Bebb, J. Amer. Chem. Soc. 61, 109 (1939); H. Gilman and F. J. Webb, ibid. 71, 4062 (1949); b) D. Seebach and N. Peleties, Angew. Chem. 81, 465 (1969); Angew. Chem. internat. Edit. 8, 450 (1969); Chem. Ber. 105, 511 (1972).

^[5] D. N. Jones, D. Mundy, and R. D. Whitehouse, Chem. Commun. 1970, 86; K. B. Sharpless and R. F. Lauer, J. Amer. Chem. Soc. 95, 2697 (1973). [6] W. Dumont, P. Bayet, and A. Krief, Angew. Chem. 86, 308 (1974); Angew.

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