cis-cyclonona-1,3,5,7-tetraene (or both). Both of these highly reactive tetraenes have been implicated as intermediates, along with the all *cis*-cyclononatetraene, in the thermal isomerization of the bicyclononatriene **7**, although the mode of their formation is still a matter of conjecture.[13] It is clear, however, that **7**, in its normal state, cannot be an intermediate in the isomerization of **1**, since under the above flow pyrolysis conditions it gave, as expected, *cis*-dihydroindene **9** as the major (80%) thermal product.

While further mechanistic studies are required we would suggest the intriguing possibility of retro Diels–Alder cleavage of **1** to vibrationally excited **7** in its extended conformation, which thereupon suffers immediate symmetry-allowed electrocyclic opening to *cis*,[3] *trans*-cyclononatriene.[19]

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(7) A low intensity ion in the mass spectrum of **4a** at *m/e* 154 was attributed to trace contamination by chloride **4b**, presumably formed through halide exchange with the catalyst CuCl.

(8) Cf. J. Haywood-Farmer, R. E. Pincock, and J. I. Wells, *Tetrahedron*, **22**, 2007 (1966); M. A. Battiste and M. E. Brennan, *Tetrahedron Lett.*, 5857 (1966).

(9) The measured parent ion (M^+) mass is slightly beyond acceptable error limits due to interference by the ^{13}C isotope peak of the intense (base) $M^+ - 1$ ion; however, the flanking *m/e* 119 and 117 ions gave the correct accurate masses for the assigned structure.

(10) After the studies reported in this paper were concluded our attention was directed to a report by T. Kumagai and T. Mukai [*Chem. Lett.*, 1187 (1975)] in which these authors propose the structure **1** for the 30% component isolated from the acetone-sensitized photolysis of tricyclo[3.2.2.0^{2,4}]nona-6,8-diene (homobarrelene). Structure assignment by the Japanese workers was largely based on analysis of the NMR (100 MHz) spectrum, which we find to be essentially identical with the spectrum (60 MHz, briefly annotated in the text) of our synthetic material, thus confirming their assignment.

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(15) To our knowledge **8** has not been previously reported. Its identity follows from its NMR [($CDCl_3$) complex multiplets from δ 1.6–3.0 (allylic) and 5.5–6.4 (vinyl) in 1:1 area ratio] and UV [λ_{max} (CCl_4) 300 nm (ϵ 8000)] spectra, its extreme sensitivity to oxygen and partial conversion to indene on exposure to air, and its alternative generation on pyrolysis of **10**. In addition, the vinyl proton pattern in the NMR spectrum of **8** is essentially identical with that for 1,1-dimethyl-7,7a-dihydroindene.[13d] We thank Professor S. W. Staley for copies of the NMR and IR spectra of the latter hydrocarbon taken from the Ph.D. Thesis of T. J. Henry, University of Maryland, 1971. Indane and indene were identified by preparative GLC isolation and comparison of NMR spectra with those of authentic samples.

(16) Allylbenzene, an anticipated secondary pyrolysis product, was also detected by NMR as a minor product, but was inseparable from *cis*-dihydroindene **9** under the capillary GLC conditions utilized for product analysis. In a later run NMR analysis of the *cis*-dihydroindene component after preparative GLC collection showed <10% contamination by allylbenzene.

(17) The enriched sample of *trans*-dihydroindene **10** was secured by preparative GLC collection of the minor (15%) dihydroindene isomer obtained on pyrolysis of **7** at 75 °C. Under the GLC conditions **10** is partially isomerized to **8**.

(18) One difference noted in the pyrolysis of **10** is that the relative yield of *cis*-dihydroindene **9** is considerably reduced (<5%). We estimate the allylbenzene/**9** ratio in this case to be essentially equal from NMR analysis of the crude pyrolysis mixture.

(19) We wish to thank the National Science Foundation for financial support of this work (Grant GP-38630X) and Dr. Roy King for his assistance with the aquisition and interpretation of the mass spectrometric data.

Merle A. Battiste,* Rocco A. Fiato
Department of Chemistry, University of Florida
Gainesville, Florida 32611
Received September 13, 1977

Aryl Selenocyanates and Aryl Thiocyanates: Reagents for the Preparation of Activated Esters

Summary: Treatment of carboxylic acids with phenyl selenocyanate and phenyl thiocyanate in the presence of tri-*n*-butylphosphine affords benzeneselenol esters and benzenethiol esters, respectively.

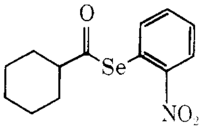
Sir: As a result of current interest in the synthesis of naturally occurring macrocyclic lactones and lactams,[1] considerable attention has been focused on the preparation of activated esters.[2,6] We wish to report a new method for the preparation of selenol esters (eq 1) and thiol esters (eq 2) which proceeds

$$\mathrm{RCOOH} \xrightarrow[\substack{\mathrm{Bu_3P} \\ \mathrm{CH_2Cl_2}}]{\mathrm{ArSeCN}} \mathrm{RCOSeAr} \tag{1}$$

$$\mathrm{RCOOH} \xrightarrow[\substack{\mathrm{Bu_3P} \\ \mathrm{CH_2Cl_2}}]{\mathrm{ArSCHN}} \mathrm{RCOSAr} \tag{2}$$

under mild conditions. During the course of examining the reaction of aryl selenocyanates with alcohols[7] and aldehydes,[8] we observed that carboxylic acids dissolved in methylene chloride or tetrahydrofuran reacted with aryl selenocyanates in the presence of tri-*n*-butylphosphine. We also demonstrated that substitution of aryl thiocyanates for aryl selenocyanates results in the formation of thiol esters.

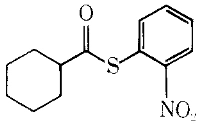
In the case of selenol esters, the reaction is best carried out employing 1.0 equiv of aryl selenocyanate and 2.0 equiv of tri-*n*-butylphosphine. The reaction can be performed on a variety of alkyl and aryl carboxylic acids (Table I) employing phenyl selenocyanate.[9] Cyclohexanecarboxylic acid, upon treatment with phenyl selenocyanate and tri-*n*-butylphosphine in methylene chloride, gave rise to an 88% yield of pure activated ester. Yields of pure isolated benzeneselenol esters are generally high (Table I). Reaction of *p*-chlorobenzoic acid with phenyl selenocyanate under the conditions described above gave rise to only a 36% yield of product, with the major product (54%) being diphenyl diselenide. Utilization of *o*-



1

$BrCH_2(CH_2)_5COSC_6H_5$

2



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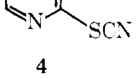

4

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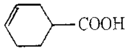
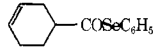
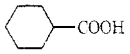
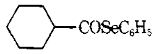
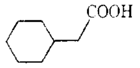
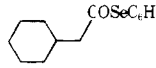
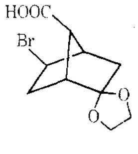
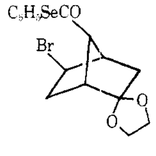
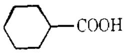
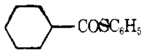
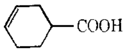
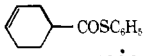
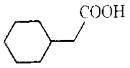
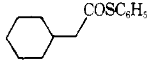
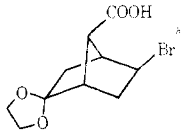
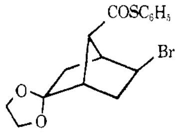
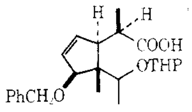
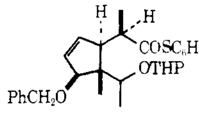
Table I. Synthesis of Benzeneselenol Esters[a]

Starting acid	Time, h	Selenol ester	Isolated yield, %	Mp, °C [Bp, °C (mm)]
CH_3COOH[b]	2.5	$CH_3COSeC_6H_5$	79	[80 (0.5)]
C_6H_5COOH	2.0	$C_6H_5COSeC_6H_5$	84	37–38
$CH_3(CH_2)_6COOH$	3.0	$CH_3(CH_2)_6COSeC_6H_5$	78	[140–143 (1.0)]
p-$CH_3OC_6H_4COOH$	0.5	p-$CH_3OC_6H_4COSeC_6H_5$	83	62–63
p-ClC_6H_4COOH	0.3	p-$ClC_6H_4COSeC_6H_5$	36[d]	83.5–84.5
	3.5		84	[119–124 (0.16)]
	2.0		88	[118–123 (0.12)]
	3.0		78	[148 (1.0)]
	3.0		46	123–125

[a] All reactions were carried out at room temperature in methylene chloride, using 1.0 equiv of phenyl selenocyanate and 2.0 equiv of tri-n-butylphosphine, unless stated otherwise. [b] This reaction was performed in tetrahydrofuran. [c] 2 equiv of phenyl selenocyanate were utilized. [d] A 54% yield of diphenyl diselenide was isolated.

Table II. Synthesis of Benzenethiol Esters[a]

Starting acid	Thiol ester	Isolated yield, %	MP, °C [Bp, °C (mm)]
CH_3COOH	$CH_3COSC_6H_5$	92	[52–54 (0.16)]
C_6H_5COOH	$C_6H_5COSC_6H_5$	96	55–56
$C_6H_5CH_2COOH$	$C_6H_5CH_2COSC_6H_5$	94	33.0–33.5
$CH_3(CH_2)_6COOH$	$CH_3(CH_2)_6COSC_6H_5$	81	[118–119 (0.1)]
p-$CH_3OC_6H_4COOH$	p-$CH_3OC_6H_4COSC_6H_5$	96	94–95
p-ClC_6H_4COOH	p-$ClC_6H_4COSC_6H_5$	92	79.5–81.5
$BrCH_2(CH_2)_5COOH$	$BrCH_2(CH_2)_5COSC_6H_5$	80	[149–153 (0.07)]
		91	[106–107 (0.07)]
		92	[117–118 (0.07)]
		96	[114–116 (0.14)]
		86	127–128
		43	

[a] All reactions were carried out at room temperature for 30 min in methylene chloride employing 1.0 equiv of phenyl thiocyanate and 1.1 equiv of tri-n-butylphosphine, unless stated otherwise. [b] C_6H_5SCN (1 equiv), Bu_3P (1.5 equiv), 3.0 h. [c] C_6H_5SCN (1.5 equiv), Bu_3P (1.5 equiv), 3.0 h.

nitrophenyl selenocyanate led to disappointingly low yields of product. For example, cyclohexanecarboxylic acid provided only a 30% yield of ester **1**.

With respect to aryl thiocyanates, the conversion of carboxylic acids into thiol esters was best performed employing 1.0 equiv of thiocyanate and 1.1 equiv of trialkylphosphine. As illustrated in Table II reaction of 7-bromoheptanoic acid with phenyl thiocyanate and tri-n-butylphosphine gave an 80% yield of thiol ester **2**. Unlike our experience above with o-nitrophenyl selenocyanate, o-nitrophenyl thiocyanate (1.2 equiv) reacted with cyclohexanecarboxylic acid in tetrahedrofuran (4 h, 25 °C) in the presence of tri-n-butylphosphine (1.2 equiv) and triethylamine (1.2 equiv), providing after workup an 86% yield of thiol ester **3**. The preparation of the 2-pyridinethiol ester of cyclohexaneacetic acid utilizing thiocyanate **4**[10] was not successful.

General Procedure for the Preparation of Benzenethiol Esters. To a solution of tri-n-butylphosphine (1.11 g, 5.5 mmol) and carboxylic acid (5.0 mmol) in 20 mL of dry methylene chloride under an atmosphere of nitrogen was added in one portion phenyl thiocyanate[11] (676 mg, 5.0 mmol) dissolved in 10 mL of methylene chloride. Upon addition the reaction mixture turns pale yellow. After anywhere from 0.5 to 3.0 h at room temperature, the solvent was removed in vacuo and the residue was chromatographed on silica gel to remove tributylphosphine oxide and minor impurities. Isolated yields of products are given in Table II for several examples.

Acknowledgment. This research was supported by the National Cancer Institute DHEW (CA 13689-06).

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(2) Recent reports in the literature have described the synthesis of selenol esters by reaction of (a) carboxylic acid–imidazoles with aliphatic and aromatic selenols,[3,4] (b) carboxylic acid–1,2,4-triazoles with selenols,[3] (c) cyclohexanecarboxylic acid diethylphosphoric anhydride, acid chloride, or imidazole with the Tl(I) salt of benzeneselenol,[5] and (d) cyclohexanecarboxylic acid with benzeneselenenyl chloride or diphenyl diselenide in the presence of tri-*n*-octylphosphine.[5]
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(5) See footnotes 3 and 17 in ref 6i.
(6) For recent reports describing the synthesis of thiol esters see: (a) E. J. Corey and D. J. Beames, *J. Am. Chem. Soc.*, **95**, 5829 (1973); (b) T. Mukaiyama, T. Takeda, and K. Atsumi, *Chem. Lett.*, 187 (1974); (c) S. Masamune, S. Kamata, J. Diakur, Y. Sugihara, and G. S. Bates, *Can. J. Chem.*, **53**, 3693 (1975); (d) T. Mukaiyama, *Angew. Chem., Int. Ed. Engl.*, **15**, 94 (1976); (e) F. Souto-Bachiller, G. S. Bates, and S. Masamune, *J. Chem. Soc., Chem. Commun.*, 719 (1976); (f) R. P. Hatch and S. M. Weinreb, *J. Org. Chem.*, **42**, 3960 (1977); (g) S. Masamune, S. Kamata, and W. Schilling, *J. Am. Chem. Soc.*, **97**, 3515 (1975); (h) H.-J. Gais, *Angew. Chem., Int. E. Engl.*, **16**, 244 (1977); (i) S. Masamune, Y. Hayase, W. Schilling, W. K. Chan, and G. S. Bates, *J. Am. Chem. Soc.*, **99**, 6756 (1977); (j) S. Yamada, Y. Yokoyama, and T. Shioiri, *J. Org. Chem.*, **39**, 3302 (1974).
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(11) F. Challenger, C. Higginbottom, and A. Huntington, *J. Chem. Soc.*, 26 (1930).
(12) Fellow of the Alfred P. Sloan Foundation.

Paul A. Grieco,*[12] Yuusaku Yokoyama
Eric Williams
Department of Chemistry, University of Pittsburgh
Pittsburgh, Pennsylvania 15260

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Favored Reduction of α-Chlorosilanes vs. α-Chloroalkanes with Tri-*n*-butyltin Hydride

Summary: The reduction of 1-chloro-2,2-dimethyl-2-silapropane, neopentyl chloride, and 1,6-dichloro-2,2,5,5-tetramethyl-2-silahexane with tri-*n*-butyltin hydride under free-radical conditions is described.

Sir: In 1965 it was suggested that α-silyl radicals may be specially stabilized compared to their all-carbon analogues, possibly by vicinal (d-p) π overlap.[1] Such stabilization was invoked to explain the absence of rearrangement in α-silyl radicals.[2] Although ESR studies appear to confirm this stabilization,[3] it seemed desirable to investigate it further. We describe here external and internal competition studies that show the heretofore unreported *preferential reduction of certain α-chlorosilanes over their all-carbon analogues* with tri-*n*-butyltin hydride. These results strongly suggest that some α-silyl radicals are indeed more stable than their all-carbon congeners.

In the external competition, mixtures of 1-chloro-2,2-dimethyl-2-silapropane ("silaneopentyl chloride", **1**) and neopentyl chloride (**2**) were dissolved in dry benzene, sealed in ampules after degassing, and reduced with tri-*n*-butyltin hydride,[4] using di-*tert*-butyl peroxide as the free-radical initiator. The results are given in Table I.

Table I. Competitive Reduction of 1 and 2[a]

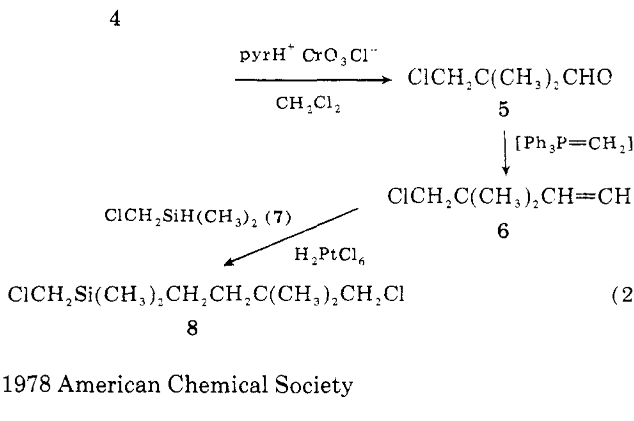
Ratio 1/2, mM	k_{Si}/k_C[b,c]
1:2[d]	78
1:1.5[d]	81

[a] On a 10–20 mmol scale. In benzene at 151–152 °C for 20 h. Ratio of materials (**1** + **2**)/tri-*n*-butyltin hydride/di-*tert*-butyl peroxide = 10:3:1. [b] Competitive rate ratio, calculated from calibrated initial and final ^1H NMR spectra by a standard method (M. J. Hutchinson and M. W. Mosher, *J. Chem. Educ.*, **48**, 629 (1971)). The results are for several runs and are ±3%. [c] The reductions afforded tetramethylsilane from **1** and neopentane from **2**, each in >90% yield. [d] Excess **2** was employed to increase the precision of the results.

It may be seen that **1** is nearly two orders of magnitude faster in this reduction than is **2**. Because the chlorine abstraction step (eq 1) determines the rate of these reductions,[5] it would appear that $(CH_3)_3SiCH_2\cdot$ (**1·**) is more easily formed than $(CH_3)_3CCH_2\cdot$ (**2·**) and therefore that **1·** might be more stable than **2·**. External competition experiments can be misleading, however. The competitive rate ratio, which only measures the relative activation barriers, might actually reflect a less stable reactant (i.e., **1**) rather than a more stable intermediate (i.e., **1·**).

$$\begin{tikzcd}[column sep=large] (CH_3)_3MCH_2Cl + \cdot Sn(n\text{-}C_4H_9)_3 & \\ \begin{array}{l} \mathbf{1}, M = Si \\ \mathbf{2}, M = C \end{array} \arrow[r, "k_{Cl}", "\text{slow}"'] & (CH_3)_3MCH_2\cdot + ClSn(n\text{-}C_4H_9)_3 \arrow[d, "\text{fast}"', "HSn(n\text{-}C_4H_9)_3"] \\ & (CH_3)_3MCH_3 \end{tikzcd} \qquad (1)$$

Because literature data applicable to the free-energy content of **1** appear to vary significantly,[6] another approach to the selectivity in eq 1 was used, viz., internal competition. Here the problem of possible ground-state-energy differences between reactants disappears. The model chosen was 1,6-dichloro-2,2,5,5-tetramethyl-2-silahexane (**8**). Its synthesis (eq 2) commenced with the oxidation of the chloro alcohol **4** (Aldrich) to the chloro aldehyde **5**: pyridinium chlorochromate in methylene chloride;[12] 80% yield; bp ~100 °C (150 mm) (Kugelrohr); 2,4-DNP, mp 137–138 °C. Anal. Calcd for $C_{11}H_{13}ClN_4O_4$: N, 18.63. Found: N, 18.69. Conversion of aldehyde **5** to olefin **6** was accomplished via the Wittig reaction: dimsyl sodium;[13] methyltriphenylphosphonium bromide (or tosylate[14]); 30% yield; bp 108–109 °C (atm); ^1H NMR (CCl_4) δ 5.83, 5.12, 4.90 ($-CH{=}CH_2$) (ABX, $J_{trans} = 18$, $J_{cis} = 9$, $J_{gem} = 3$ Hz), 3.30 (s, $-CH_2Cl$), 1.10 (s, $-CH_3$); IR (neat) 3110, 1642, 928 ($-CH{=}CH_2$), 1382, 1368 (CH_3) cm^{-1}. Anal. Calcd for $C_6H_{11}Cl$: C, 60.76; H, 9.35. Found: C, 61.08; H, 9.50. Addition of silane **7**[15] to **6** in the presence of chloroplatinic acid afforded **8**: 71% yield, collected by GLC on DC-200 at 150 °C; ^1H NMR (CCl_4) δ 3.33 (s, $>CCH_2Cl$), 2.73 (s, $>SiCH_2Cl$), 1.53—1.17 (m, $>SiCH_2CH_2C<$), 0.97 (s, $>C(CH_3)_2$), 0.70–0.30 (m, $>SiCH_2CH_2C<$), 0.13 (s, $>Si(CH_3)_2$); IR (neat) 1390, 1370 ($>C(CH_3)_2$), 1260 ($>Si(CH_3)_2$) cm^{-1}. Anal. Calcd for $C_9H_{20}Cl_2Si$: C, 47.57; H, 8.87. Found: C, 47.83; H, 8.89.



(2)