Table V

expt	wt of 4 used,g (mmol)	wt of CsF used, g (mmol)	solvent (amount, mL)	time	final *exo*-4/*endo*-4 ratio
1	0.10 (0.79)	0.07 (0.49)	DMF (0.5)	2 h	56:44
2	0.10 (0.79)	0.08 (0.56)	DMF (0.5)	2 h	55:45
3	0.02 (0.16)	0.01 (0.07)	CD_3CN (0.4)	7 days	54:46
4 (control)	0.10 (0.79)	none	DMF (0.5)	7 days	80:20

ratio of **3a**/**3b**. A similar reaction using half the concentration of reagents proceeded at a slower rate with the same overall result.

Free-Radical Chlorination of 4. NMR Tube Reaction. A solution of **4a**/**4b** (41 mg, 0.33 mmol) and benzoyl peroxide (5.7 mg, 0.024 mmol) in 0.4 mL of carbon tetrachloride was heated at 82 °C for 22 h; ^1H NMR analysis showed that most of the reaction had occurred after 12 h. The isomer ratio of starting material was 81:19 **4a**/**4b**; the isomer ratio of the product was 77:23 **3a**/**3b**. No other product was observed.

Preparative Scale Reaction. A solution of **4a**/**4b** (1.3 g, 10 mmol) in 30 mL of carbon tetrachloride was stirred at reflux temperature for 2.5 days; benzoyl peroxide (80 mg, 0.33 mmol) was added in two 30-mg and one 20-mg increments to effect complete reaction. The isomer ratio for **3** at the end of reaction was 77:23 **3a**/**3b**. Most of the solvent was removed by bulb-to-bulb distillation at reduced pressure; the distillation pot was maintained at 0 °C, and the receiver was cooled in dry ice; the minimum pressure was 44 mm. The residue (ca. 4 g) consisted of **3a** and **3b** in the same ratio determined above plus carbon tetrachloride and traces of aromatic material; no other silicon-containing product was observed by ^1H NMR or GC analysis. Two 0.4-mL aliquots from this residue were placed in NMR tubes; one was kept at room temperature. To the other was added an equal volume of ether. No isomerization nor decomposition was observed for either sample over 4 days at room temperature.

LAH Reduction of the Crude Product from the Free-Radical Chlorination Reaction. To LAH (2.6 g, 68 mmol) in 125 mL of ether at −25 °C was added crude **3** (77:23 **3a**/**3b**, from the previous experiment) in 40 mL ether over a period of 20 min. This mixture was stirred for 1.5 h while being allowed to warm to 5 °C and then was stirred for 30 min. The reaction mixture was slowly poured onto 400 mL of 10% H_2SO_4 and ice overlaid with 100 mL of pentane, worked up, and distilled as previously described to give 0.80 g of a clear, colorless liquid. ^1H NMR, ^{13}C NMR, and GC analyses showed this to be **4a**/**4b** (67:33).

Equilibration Studies of 4 with CsF. Three equilibration experiments were performed in NMR tubes by using the quantity of materials shown in Table V; **4** was purified by preparative GC, and the starting isomer ratio was 80:20 **4a**/**4b** in each case. All reactions were run at room temperature. Prolonged reaction times (>5 h) for expts 1 and 2 indicated decomposition of starting **4**. Experiment 3 was observed for 3 days after equilibrium had been attained; there was no change in the isomer ratio. Subsequently it was analyzed by GC and then transferred to a ^{13}C NMR tube, rinsing with $CDCl_3$. The ^{13}C NMR spectrum only showed major peaks due to the isomers of **4**.

Acknowledgment. We thank Cerac, Inc., of Milwaukee, WI, for the gift of CsF. C.B. thanks the Society of Sigma Xi for partial support of this research. We also acknowledge partial support of this project from NATO grant No. RG206.80 and to our collaborator, Dr. J. P. Albrand, for the ^{29}Si NMR data. We thank the NSF for Grant TFI 8020268 used to purchase a Varian EM 360 L 60-MHz NMR spectrometer.

Registry No. 1, 37871-86-6; **2**, 80864-28-4; **3a**, 80864-29-5; **3b**, 80864-30-8; **4a**, 80864-31-9; **4b**, 80864-32-0; **5**, 14320-38-8; **6**, 36367-85-8; **7**, 4492-41-5; **8**, 7686-77-3; **9**, 25125-21-7; **9** tosylate, 25125-22-8; **10**, 80864-33-1; **11**, 80864-34-2; **12**, 80864-35-3; 9-BBN, 25301-61-5; cyclopentadiene, 542-92-7.

α Vinylation of Ketones. A General Method Using (Phenylseleno)acetaldehyde

Derrick L. J. Clive,* Charles G. Russell,[†] and Suresh Chander Suri

Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada T6G 2G2

Received July 21, 1981

(Phenylseleno)acetaldehyde can be used as a synthetic equivalent of the vinyl carbonium ion, $CH_2{=}CH^+$. A number of ketone enolates, usually as zinc salts, were condensed with (phenylseleno)acetaldehyde to give β-hydroxy selenides (average yield 78% for 10 examples). Treatment of these substances with methanesulfonyl chloride and triethylamine afforded the corresponding α-vinyl ketones (average yield 72% for 10 examples). This methodology provides access to compounds that are correctly constituted to undergo Cope and oxy-Cope rearrangements. The sequences **1a** → **1e** and **8a** → **8d** are illustrative. Introduction of α-isopropenyl groups is also feasible by using (phenylseleno)acetone in the initial condensation step.

We report here details of our experiments on the use of (phenylseleno)acetaldehyde as a synthetic equivalent of the vinyl carbonium ion, $CH_2{=}CH^+$.[1] The use of this selenium reagent to convert ketones into β,γ-unsaturated ketones (Scheme I, X = PhSe) represents a new route, discovered independently in two laboratories,[1] to substances that are properly constituted to undergo Cope,[2] oxy-Cope,[3] and Cope–Claisen[4] rearrangements (Scheme II).[5]

Such electrocyclic processes are, of course, permanently established as synthetic methods of considerable impor-

---

[†] Natural Sciences and Engineering Research Council of Canada Postgraduate Scholar.

(1) (a) Clive, D. L. J.; Russell, C. G. *J. Chem. Soc., Chem. Commun.* **1981**, 434. (b) Kowalski, C. J.; Dung, J.-S. *J. Am. Chem. Soc.* **1980**, *102*, 7950.

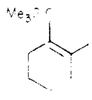
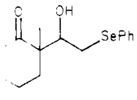
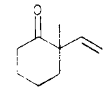
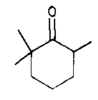
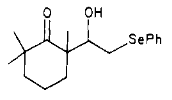
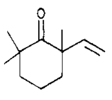
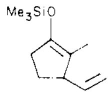
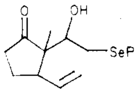
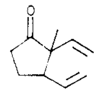
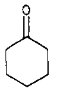
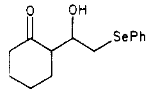
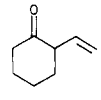
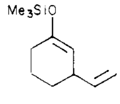
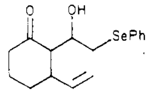
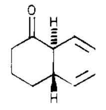
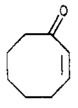
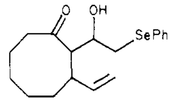
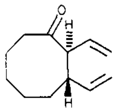
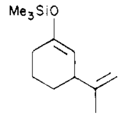
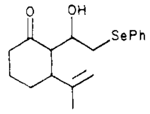
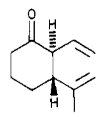
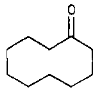
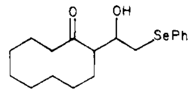
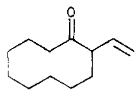
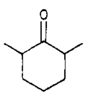
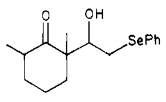
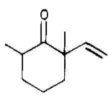
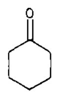
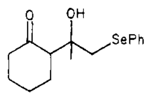
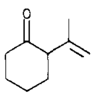
(2) (a) Rhoads, S. J.; Raulins, N. R. In "Organic Reactions"; Dauben, W. G., Ed.; Wiley: New York, 1975; Vol. 22, Chapter 1. (b) Evans, D. A.; Baillargeon, D. J.; Nelson, J. V. *J. Am. Chem. Soc.* **1978**, *100*, 2242 and references therein.

(3) (a) Berson, J. A.; Gajewski, J. J. *J. Am. Chem. Soc.* **1964**, *86*, 5019. (b) Evans, D. A.; Golob, A. M. *Ibid.* **1975**, *97*, 4765. (c) Still, W. C. *Ibid.* **1977**, *99*, 4186.

(4) (a) Ziegler, F. E.; Piwinski, J. J. *J. Am. Chem. Soc.* **1980**, *102*, 880. (b) *Ibid.* **1979**, *101*, 1612.

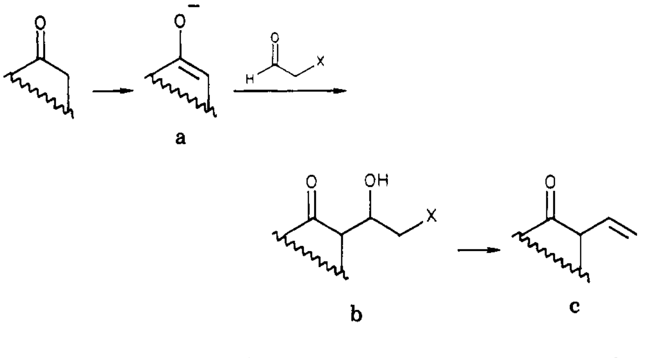
0022-3263/82/1947-1632$01.25/0

Table I[a]

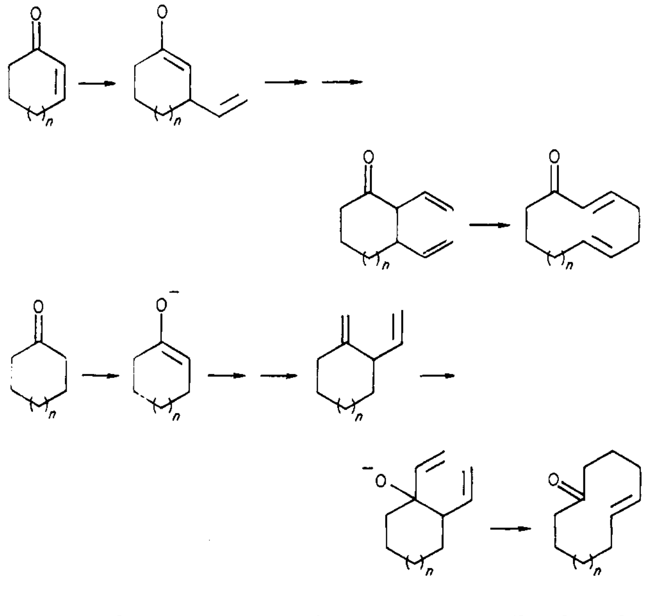
expt	starting matl	condensation product (yield, %)	olefin (yield, %)	expt	starting matl	condensation product (yield, %)	olefin (yield, %)
1	 1a	 1b (95)[b]	 1c (82,[c] 78[c,d])	6	 6a	 6b (75)[b]	 6c (84,[l,m] 98[d])
2	 2a	 2b (83)[b]	 2c (82,[e] 84[f])	7	 7a	 7b (78)[b]	 7c (54)[l,n]
3	 3a	 3b (90)[b]	 3c (82)[g]	8	 8a	 8b (34)[o]	 8c (68)[p]
4	 4a	 4b (89)[h]	 4c (89,[i] 80[j])	9	 9a	 9b (85)[q]	 9c (50)[r]
5	 5a[b]	 5b (89)[b]	 5c (75)[k,l]	10	 10a	 10b (67)[b]	 10c (62,[l,n] 91[s])

[a] Yields refer to isolated material, except where indicated. Except for structures 3c, 4c, and 8c, the formulas are not intended to have stereochemical implications. No attempts were made to optimize the yields of 2a (38%, lit.[37] 89%), 3a (39%), and 4a (86%). [b] Mixture of diastereoisomers. [c] The precursor was the crystalline diastereoisomer. [d] $COCl_2$-NaI method. Yield determined by NMR. [e] 97% pure by VPC. High-R_f hydroxyselenide used. [f] 99% pure by VPC. Low-R_f hydroxyselenide used. [g] 97.5% pure by VPC. High-R_f hydroxyselenide used. [h] Combined yield of the separated isomers. [i] >99% pure by VPC. High-R_f hydroxyselenide used. [j] >98% pure by VPC. Low-R_f hydroxyselenide used. [k] >98% pure by VPC. [l] Diastereoisomeric mixture of hydroxyselenides used. [m] >99% pure by VPC. [n] Yield determined by NMR. [o] One (>97%) diastereoisomer. [p] >97% pure by VPC. [q] One (>98%) diastereoisomer. [r] >99% pure by VPC. [s] After correction for recovered starting material.

Scheme I



Scheme II



tance, and so it is likely that efficient equivalents for the vinyl carbonium ion would be useful species. They are, however, now well-known,[6] and conventional methodology for introduction of a vinyl group can entail a lengthy procedure.[4a]

Of several potential approaches[7] to synthetic equivalents

---

(5) The formulas are not intended to have stereochemical implications.

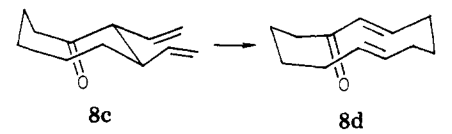
(6) (a) Procedures based on Michael addition to phenyl vinyl sulfoxide: Koppel, G. A.; Kinnick, M. D. *J. Chem. Soc., Chem. Commun.* **1975**, 473. Bruhn, J.; Heimgartner, H.; Schmid, H. *Helv. Chim. Acta* **1979**, *62*, 2630. (b) Procedure based on Michael addition to a vinyl sulfone: Metcalf, B. W.; Bonilavri, E. *J. Chem. Soc., Chem. Commun.* 1978, 914. (c) Transition-metal-catalyzed vinylation: Rathke, M. W.; Millard, A. A. *J. Am. Chem. Soc.* **1977**, *99*, 4833. (d) Cf.: Hudrlik, P. F.; Peterson, D.; Rona, R. J. *J. Org. Chem.* **1975**, *40*, 2263. Eisch, J. J.; Galle, J. E. *Ibid.* **1976**, *41*, 2615.

for the vinyl carbonium ion, one is summarized in Scheme I, in which X must be chosen to permit formation of the double bond (b → c). Conversion of β-substituted alcohols (HO–C–C–X) into olefins is a well-known process for X = Si,[8] P,[9] and Se.[10] However, there are some restrictions implicit in the scheme. For example, α-silyl aldehydes are, at present, relatively inaccessible compounds,[11] and, in our hands, preliminary experiments to effect aldol condensations with $(EtO)_2P(O)CH_2CHO$,[12] proceeded poorly.[13] Scheme I could be implemented easily, however, by using (phenylseleno)acetaldehyde,[14] and our experiments, which are summarized in Table I, have been based on this readily accessible compound.[15]

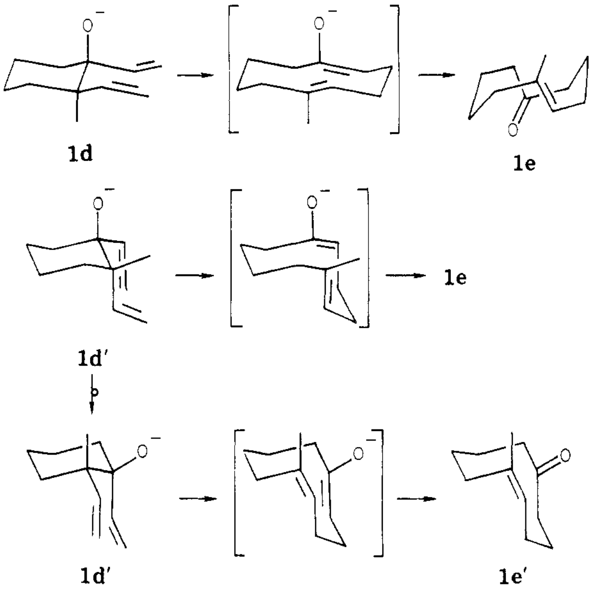
Condensations with (Phenylseleno)acetaldehyde. Zinc enolates have a favorable reputation[16] for reacting smoothly in aldol condensations and, therefore, we used these salts in most of our work.[17] (This procedure is different from that used in another study.[1b,17]) The zinc species are easily and quickly generated[16a] in situ by adding ethereal zinc chloride to a cold solution of a lithium enolate (0.5 mol of zinc chloride/mol of lithium enolate).

Our lithium enolates were prepared by well-established procedures, either by kinetic deprotonation of a ketone with LDA or by the action of methyllithium on a silyl enol ether.[18] A third route involved conjugate vinylation of an enone, and in the case of experiments 2–4, the resulting enolate species[19] were silylated (to give **2a**, **3a**, and **4a**) before proceeding with the condensation. The medium-ring enone **8a** did not undergo 1,4-vinylation efficiently.[20] In this case no advantage[19] was apparent by first silylating the enolate derived by the conjugate addition, and we and others[1b] have found it possible to use such enolates directly for the condensation.[21]

Scheme III



Scheme IV



Finally, we found that a boron enolate[22] may also be employed. Here, release of the condensation product involves, as an additional step, treatment with trimethylamine N-oxide,[23] but this requirement is offset by the fact that there are some instances[24] where regiochemically pure enol derivatives are readily assembled in the form of enol borinates.

We experienced no difficulties[16b] in isolating and handling the keto hydroxy–selenide condensation products. The reactions were clean and, although we always purified these compounds, it is not essential to do so.[25]

It was sometimes possible to separate the isomeric hydroxy selenides. The stereochemistry at the hydroxyl-bearing carbon is not relevant to the overall transformation because that center is eventually converted to sp^2 hybridization, and in examples **2b**, **3b**, and **4b** where we examined such isomers individually, we noticed no substantive difference in the ease of generating the double bond although one isomer did react a little faster (TLC control) than the other. The stereochemistry may actually be subject to a certain amount of experimental control: We

---

[7] For a method based on dicarbonyl-η^5-cyclopentadienyliron η^2-vinyl ether complexes see: Chang, T. C. T.; Rosenblum, M.; Samuels, S. B. *J. Am. Chem. Soc.* **1980**, *102*, 5930.

[8] Peterson, D. J. *J. Org. Chem.* **1968**, *33*, 780. Colvin, E. W. *Chem. Soc. Rev.* **1978**, *7*, 15.

[9] Cadogan, J. I. G., Ed. "Organophosphorus Reagents in Organic Synthesis"; Academic Press: New York, 1979.

[10] Review: Clive, D. L. J. *Tetrahedron* **1978**, *34*, 1049.

[11] Me_3SiCH_2CHO: Zaitsega, G. S.; Chernyavskii, A. I.; Baukov, Y. I.; Lutsenko, I. F. *J. Gen. Chem. USSR (Engl. Transl.)* **1976**, *46*, 840; *Zh. Obschch. Khim.* **1976**, *46*, 843. Ph_3SiCH_2CHO: Eisch, J. J.; Trainor, J. T. *J. Org. Chem.* **1963**, *28*, 2870. This compound condenses (ca. 60% yield) in the sense of Scheme I when treated with the dibutyl[(cyclohex-1-enyl)oxy]borane (see the Experimental Section for preparation of the borane).

[12] Preparation: Razumov, A. I.; Moskva, V. V. *J. Gen. Chem. USSR (Engl. Transl.)* **1964**, *34*, 2612; *Zh. Obshch. Khim.* **1960**, *34*, 2589. Razumov, A. I.; Savicheva, G. A. *J. Gen. Chem. USSR (Engl. Transl.)* **1964**, *34*, 2617; *Zh. Obshch. Khim.* **1964**, *34*, 2595.

[13] The condensations were tried with dibutyl[(cyclohex-1-enyl)oxy]borane (see the Experimental Section for preparation of the borane).

[14] Preparation: Baudat, R.; Petrzilka, M. *Helv. Chim. Acta* **1979**, *62*, 1406.

[15] Preliminary experiments with $MeSeCH_2CHO$ gave low yields of aldol products. The aldehyde was prepared by the sequence below and had the following: IR (neat) 1704 cm^{-1}; NMR ($CDCl_3$, 200 MHz) δ 1.87 (s, 3 H), 3.10 (d, J = 4 Hz, 2 H), 9.30 (t, J = 4 Hz, 1 H); exact mass, m/e 137.9587 (calcd for $C_3H_6O^{80}Se$, m/e 137.9587). The condensations were tried with dibutyl[(4-*tert*-butylcyclohex-1-enyl)oxy]borane and with the enolate (LDA) of cyclododecanone.

$$Me_2Se_2 \xrightarrow[EtOH]{NaBH_4} MeSe^- \xrightarrow{ClCH_2CH(OEt)_2} MeSeCH_2CH(OEt)_2 \xrightarrow{H_3O^+} MeSeCH_2CHO$$

[16] (a) House, H. O.; Crumrine, D. S.; Teranishi, A. Y.; Olmstead, H. D. *J. Am. Chem. Soc.* **1973**, *95*, 3310. (b) Heng, K. K.; Smith, R. A. J. *Tetrahedron* **1979**, 425. (c) Näf, F.; Decorzant, R. *Helv. Chim. Acta* **1974**, *57*, 1317.

[17] The independent studies[1b] show that generation of zinc enolates, though an easy step from the corresponding lithium salt, may, in general, be an unnecessary precaution.

[18] Use of silyl enol ethers permits generation of the thermodynamically more stable of two isomeric enolates, e.g., **1a**.

[19] Enolates derived by 1,4 cuprate addition sometimes have a different degree of reactivity from ordinary enolates,[16b] and we usually bypassed this potential complication by using silyl enol ethers.

[20] Cf.: Camus, A.; Diara, A.; Damiano, J.-C. *C. R. Hebd. Seances Acad. Sci., Ser. C* **1975**, *280*, 523. Mookherjee, B. D.; Trenkle, R. W.; Patel, R. R. *J. Org. Chem.* **1971**, *36*, 3266. Mookherjee, B. D.; Patel, R. R.; Ledig, W. O. *Ibid.* **1971**, *36*, 4124. For effect of solvent see: House, H. O.; Respess, W. L.; Whitesides, G. M. *Ibid.* **1966**, *31*, 3128.

[21] In this example we did not use $ZnCl_2$.

[22] Certain enol borinates can be made by 1,4-addition of trialkylboranes to enones: Brown, H. C.; Rogic, M. M.; Rathke, M. W.; Kabalka, G. W. *J. Am. Chem. Soc.* **1967**, *89*, 5709.

[23] Hooz, J.; Mortimer, R. D. *Can. J. Chem.* **1978**, *56*, 2786.

[24] E.g.: Masamune, S.; Mori, S.; Van Horn, D.; Brooks, D. W. *Tetrahedron Lett.* **1979**, 1665. Hooz, J.; Linke, S. *J. Am. Chem. Soc.* **1968**, *90*, 5936.

[25] E.g., The overall yield for **4a** → **4c** without purification of **4b** is 72%. If **4b** is purified the overall yield is 76%.

noticed, for example, with **1b** and **7b** that the isomer proportion varies with reaction time, but the other examples were not studied in this regard.

A stereochemical feature that is important, however, is the relationship (cis or trans) of the substituents attached to the ring when the enolate is generated by 1,4-vinylation of an enone. In the cases we examined (**3b**, **4b**, and **8b**) the vinyl and 1-hydroxy-2-(phenylseleno)ethyl groups were trans.[26] This result is relevant to subsequent Cope rearrangement, e.g., **8c** → **8d** (Scheme III).

Finally, condensation with (phenylseleno)acetone[27] (entry 10, Table I) is also possible, and it provides a method for isopropenylation (**7a** → **10b** → **10c**).

Generation of the Double Bond. One reason for selecting (phenylseleno)acetaldehyde in the present work was the fact that a considerable variety of procedures are known[10] for converting β-hydroxy selenides into olefins. We tried several of the published methods[28] as well as some potential new ones,[29] but of those we examined, only the reaction of methanesulfonyl chloride in the presence of triethylamine[30] was generally useful. We also found that treatment of β-hydroxy selenides with phosgene in the presence of pyridine (in ether solution at room temperature) and exposure of the derived chloroformate to sodium iodide in acetonitrile afford olefins, but, of several cases (using the present series of β-hydroxy selenides) in which we made a comparison, only **6c** and **1c** were formed efficiently by this method. Our impression (based upon spectroscopically determined yields) is that the elimination with methanesulfonyl chloride almost always proceeds efficiently and that the variation in yield of required olefin is a consequence of the tendency for β,γ-unsaturated ketones to isomerize to the conjugated analogues. 2-Vinylcyclohexanone and the medium-ring ketone **9c** were particularly sensitive in this respect,[31] while the presence of an additional substituent (excluding cases where conjugation is blocked) as in **3c**, **4c**, and **8c** appears to discourage isomerization.

Application to Cope and Related Rearrangements. When the diene **8c** is heated at 200 °C it undergoes smooth Cope rearrangement in 90% yield (Scheme III). The process is evidently favored by the fact that it involves conversion of a medium-ring into a large-ring system with the attendant release of transannular interactions. Cope rearrangement of **4c**, which would involve expansion of a normal- into a medium-ring system, was not successful under the same conditions, and only conjugation of the double bond (from the 2-vinyl substituent) was observed.[32] The stereochemical outcome for the process **8c** → **8d** can be rationalized in terms of a reacting conformation such as that shown (Scheme III).[33]

When the α-blocked ketone **1c** was treated with vinylmagnesium bromide, the two isomers **1d** and **1d′** (Scheme IV) were formed, as expected, and the derived potassium alkoxides underwent smooth oxy-Cope rearrangement[3] in refluxing THF. One isomer gave **1e** plus 3% of the corresponding *Z* olefin, **1e′**, while the other isomer gave only (>99%) **1e**. On the basis of chair transition states for the rearrangement, these facts can be interpreted as in Scheme IV.[34]

Conclusion

(Phenylseleno)acetaldehyde is a general reagent for efficient condensation with ketone enolates. The resulting hydroxy selenides are converted into β,γ-unsaturated ketones in a process that is straightforward if the α-position is blocked or the ketone has additional substituents that hinder conjugation. Use of (phenylseleno)acetone renders possible access to isopropenyl groups. The above methodology can be combined with copper-mediated conjugate addition to provide access to substances suitable for Cope and Cope–Claisen rearrangement. The products of Cope rearrangement, e.g., **8d**, are α,β-unsaturated ketones and, in principle, they are amenable to repetition of the ring-expansion process.

In suitable cases, e.g., **1c**, treatment of the α-vinyl ketone with a vinyl *carbanion* gives a product which will undergo ring expansion via an oxy-Cope rearrangement.

Experimental Section

Except where stated to the contrary, the following particulars apply. Experiments were done with magnetic stirring under a slight static pressure of nitrogen, purified by passage through a column (3.5 × 42 cm) of R-311 catalyst[35] and then through a similar column of Drierite. Inlet and exit needles for nitrogen were passed through a septum on the apparatus, and after a few minutes (provided no gas was to be generated in the reaction) the exit needle was removed so as to keep the contents of the

---

[26] For example: **4b** (high R_f), **4b** (low R_f), and **8b** contained less than 1% of the corresponding cis isomer; **3b** (high R_f) contained less than 2%.

[27] (a) Preparation: Sharpless, K. B.; Lauer, R. F.; Teranishi, A. Y. *J. Am. Chem. Soc.* **1973**, *95*, 6137. Ryu, I.; Murai, S.; Niva, I.; Sonoda, N. *Synthesis* **1977**, 874. (b) After submission of this manuscript an alternative method for isopropenylation was published: Chang, T. C. T.; Rosenblum, M. *J. Org. Chem.* **1981**, *46*, 4103.

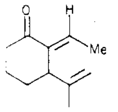
[28] The following reagents were used under conditions specified in the literature:[10] NaH/*o*-phenylene phosphorochloridite; Et_3N/trifluoroacetic anhydride; $Et_3N/SOCl_2$.

[29] NaH/trifluoroacetic anhydride/NaI/1:1 THF–MeCN/room temperature; *t*-BuLi/trifluoroacetic anhydride/NaI/THF/room temperature; *i*-$Pr_2NEt/SOCl_2/CH_2Cl_2$/room temperature; *n*-BuLi/HMPA/$SOCl_2$/NaI/−20 °C/1:2 ether–MeCN; pyridine/$SOCl_2/CH_2Cl_2$/room temperature; Me_3SiCl/NaI/MeCN/room temperature; Me_3SiCl/pyridine/NaI/MeCN/room temperature; 1-(trimethylsilyl)-1*H*-imidazole/CH_2Cl_2/room temperature; Et_3N/1-ethyl-2-fluoropyridinium tetrafluoroborate/LiI/acetone 65 °C (Mukaiyama, T.; Imaoka, M. *Chem Lett.* **1978**, 413); pyridine/*S*-phenyl carbonochloridothioate/CH_2Cl_2/room temperature; NaH/*O*-(3-chlorophenyl)carbonochloridothioate/THF/room temperature (Garmaise, D. L.; Uchiyama, A.; McKay, A. F. *J. Org. Chem.* **1962**, *27*, 4509); *O*-(3-chlorophenyl)carbonochloridothioate/4-(dimethylamino)pyridine/Et_2O/room temperature, then 110 °C without solvent; $Et_3N/CF_3SO_2Cl/CH_2Cl_2$/0 °C.

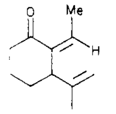
[30] Reich, H. J.; Chow, F.; Shah, S. K. *J. Am. Chem. Soc.* **1979**, *101*, 6638.

[31] 2-Ethenylcyclododecanone is far *less* sensitive in this respect. Preparation: [(1-cyclododecen-1-yl)oxy]trimethylsilane → 2-[1-hydroxy-2-(phenylseleno)ethyl]cyclododecanone (ca. 71%) → 2-ethenylcyclododecanone (ca. 75%).

[32] Compound i: 100% pure by VPC; IR (neat) 1687 cm^{-1}; NMR ($CDCl_3$, 200 MHz) δ 1.62–2.08 (m, including a d at 1.69, J = 7.6 Hz, and s at δ 1.80 split by unresolved coupling, 10 H), 2.17–2.59 (m, 2 H), 3.42–3.54 (m, 1 H), 4.50–4.59 (m, 1 H), 4.82–4.90 (m, 1 H), 6.82 (q d, J = 7.2, 1.2 Hz, 1 H); exact mass, *m/e* 164.1202 (calcd for $C_{11}H_{16}O$, *m/e* 164.1201). Compound ii: >99% pure by VPC (94.5% one isomer, 5.1% of the above isomer); IR ($CDCl_3$) 1687 cm^{-1}; NMR ($CDCl_3$, 200 MHz), 1.66–2.14 (m, including an s at δ 1.72 split by unresolved coupling and a dd at δ 1.93, J = 7.2, 1.2 Hz, 10 H), 2.24–2.58 (m, 2 H), 3.10–3.24 (m, 1 H), 4.63–4.72 (m, 1 H), 4.88–4.97 (m, 1 H), 5.73 (q d, J = 7.2, 1.1 Hz, 1 H); exact mass, *m/e* 164.1199 (calcd for $C_{11}H_{16}O$, *m/e* 164.1201).



i



ii

[33] (a) The boat–chair conformation shown for the eight-membered ring is a tentative assignment, and the conformation (but not the olefin geometry) of the twelve-membered ring is arbitrary. (b) For discussions of the conformational analysis of medium and large rings see: Dale, J. "Stereochemistry and Conformational Analysis"; Verlag Chemie: New York, 1978.

[34] (a) Marvell, E. N.; Whalley, W. *Tetrahedron Lett.* **1970**, 509. (b) For conformations of C_{10} rings see ref 33b. The conformation shown for **1e** is tentative, and that for **1e′** is arbitrary.

[35] An American supplier of this BASF catalyst is Chemical Dynamics Corp.

apparatus under a slight static pressure of nitrogen. Solvents were distilled before use for chromatography or extraction. Dry triethylamine, pyridine, pentane, dichloromethane, chlorotrimethylsilane, HMPA, and acetonitrile were distilled from CaH_2 and dry THF and ether from sodium (benzophenone indicator). Sodium iodide was dried in vacuo. During product isolation, solutions were dried (where necessary) over $MgSO_4$ and evaporated under water-pump vacuum at room temperature. Where compounds were isolated simply by evaporation of their solutions, the residues were kept under oil-pump vacuum and checked for constancy of weight. Isolated products were submitted directly for combustion analysis without additional purification. Yields evaluated by VPC were determined by using an internal standard. For VPC, the column used was as follows: 6 ft, 10% DEGS, Chromosorb W (80–100 mesh). Silica gel for column chromatography was Merck type 60 (70–230 mesh). Silica gel for flash chromatography[36] was Merck type 60 (230–400 mesh). Commercial TLC plates (Camag DF-B or Merck 60F-254) were used. Mass spectra were run at an ionizing voltage of 70 eV. Boiling points quoted for products distilled in a Kugelrohr apparatus refer to the oven temperature.

(Phenylseleno)acetaldehyde. The literature procedure[14] was followed except that phenylselenenyl *chloride* and a large (tenfold) excess of ethyl vinyl ether were used.

[(3-Ethenyl-2-methyl-1-cyclopenten-1-yl)oxy]trimethylsilane (2a). The literature procedure[37] was followed but with commercial vinyl magnesium bromide (adjusted to 0.68 M) in THF. It is important to cool the reaction mixture (to about −70 °C) *immediately* after addition of copper(I) iodide.

[(3-Ethenyl-1-cyclohexen-1-yl)oxy]trimethylsilane (3a). The initial stages employed for **2a** were followed by using vinylmagnesium bromide (34.75 mL, 0.68 M in THF), copper(I) iodide (2.43 g, 12.8 mmol), cyclohex-2-enone (1.00 g, 10.4 mmol), chlorotrimethylsilane (3.20 mL, 25.2 mmol), HMPA (6.60 mL), and triethylamine (4.73 mL, 33.9 mmol). After the 2-h warm-up period the solution was poured into a vigorously stirred mixture of pentane (50 mL), ether (50 mL), and water (50 mL). The resulting mixture was filtered. The organic phase was washed with saturated aqueous sodium hydrogen carbonate and with brine. It was then dried and evaporated. The residue was distilled [bp 72 °C (3 mm)] and subjected to flash chromatography over silica (2 × 15 cm) with 433:1 hexane–chloroform. Appropriate fractions were combined, and Kugelrohr distillation [bp 72 °C (3 mm)] gave **3a** (777 mg, 38%) as a homogeneous (TLC, silica, 433:1 hexane–chloroform), colorless liquid: IR ($CDCl_3$) 1662 cm^{-1}; NMR ($CDCl_3$, 100 MHz) δ 0.22 (s),[38] 1.1–2.1 (m, 6 H), 2.7–2.98 (br s, 1 H), 4.7–5.1 (m, 3 H), 5.58–5.96 (m, 2 H); exact mass *m/e* 196.1276 (calcd for $C_{11}H_{20}OSi$, *m/e* 196.1283). Anal. Calcd for $C_{11}H_{20}OSi$: C, 67.28; H, 10.27. Found: C, 67.46; H, 10.25. Satisfactory O or Si analyses could not be obtained. The experiment was repeated by a procedure involving the use of a catalytic amount of copper(I) iodide,[39] but the yield was not improved significantly.

[3-(1-Methylethenyl)-1-cyclohexen-1-yl)oxy]trimethylsilane (4a).[40] A few drops of 2-bromopropene were added to magnesium (537 mg, 22.1 mmol), THF (15 mL), and a crystal of iodine. When the Grignard reaction had started, more 2-bromopropene (total used = 3.66 g, 30.3 mmol) in THF (5 mL plus a 1-mL rinse) was added over 13 min, and the reaction mixture was then refuxed for 15 min. It was diluted with THF (15 mL) and cooled to 0 °C. Anhydrous copper(I) iodide (210 mg, 1.10 mmol) was added, and a solution of cyclohex-2-enone (1.00 g, 10.4 mmol) in THF (14 mL plus a 1-mL rinse) was injected with stirring over 10 min. The resulting mixture was stirred at 0 °C for an additional 1 h, and the experiment was completed as for the preparation of **2a** but at 0 °C (instead of −60 °C) by using chlorotrimethylsilane (3.20 mL, 25.2 mmol), HMPA (6.60 mL), and triethylamine (4.73 mL, 33.9 mmol). After being allowed to warm to room temperature over about 2 h, the mixture was shaken in a separatory funnel containing pentane (100 mL) and 10% w/v aqueous ammonium chloride (50 mL). The aqueous layer was extracted with ether, and the combined pentane–ether extracts were dried, evaporated, and distilled to afford **4a** (1.89 g, 86%) as a colorless, homogeneous (TLC, silica, 433:1 hexane–chloroform) liquid, better than 98% pure by VPC analysis: bp 84 °C (2.9 mm); IR (film) 1662 cm^{-1}; NMR ($CDCl_3$, 100 MHz) δ 0.2 (s),[38] 1.24–2.2 (m, 9 H), 2.7–2.95 (br, 1 H), 4.66–4.82 (m, 3 H); exact mass *m/e* 210.1438 (calcd for $C_{12}H_{22}OSi$, *m/e* 210.1439). Anal. Calcd for $C_{12}H_{22}OSi$: C, 68.51; H, 10.54. Found: C, 68.59; H, 10.60. Satisfactory O and Si analyses could not be obtained.

2-[1-Hydroxy-2-(phenylseleno)ethyl]-2-methylcyclohexanone (1b). Methyllithium (1.47 M, ether solution, 1.71 mL, 2.51 mmol) was injected at room temperature into a stirred solution of the silyl enol ether **1a**[41] (463 mg, 2.51 mmol) in ether (6 mL). After a further period of 1.5 h the mixture was cooled to 0 °C, and zinc chloride (1.82 mL of a saturated ether solution,[16a] 1.26 mmol) was added dropwise. The mixture was left for 10 min at 0 °C and (phenylseleno)acetaldehyde (500 mg, 2.51 mmol) in ether (2.5 mL plus a 0.5-mL rinse) was injected rapidly (main portion added over ca. 3 s). The mixture was stirred for a further 5 min and was then shaken with aqueous ammonium chloride (10% w/v). The ether layer was washed with saturated sodium hydrogen carbonate and with brine. It was then dried and evaporated. Flash chromatography over silica gel (5 × 15 cm) with 4:1 heptane–ethyl acetate gave **1b** (745 mg, 95%) as a pale yellow oily mixture of diastereoisomers [ca. 59:41 (NMR)] which were partially resolvable by TLC (4:1 heptane–ethyl acetate): IR ($CDCl_3$) 1693 cm^{-1}; NMR ($CDCl_3$, 200 MHz) δ 1.11 (s, 1.24 H), 1.20 (s, 1.81 H), 1.50–3.18 (m, 11 H), 3.96–4.10 (m, 1 H), 7.18–7.38 (m, 3 H), 7.48–7.64 (m, 2 H); exact mass *m/e* 312.0627 (calcd for $C_{15}H_{20}O_2{}^{80}Se$, *m/e* 312.0629). Anal. Calcd for $C_{15}H_{20}O_2Se$: C, 57.88; H, 6.48; O, 10.28. Found: C, 57.97; H, 6.44; O, 10.40.

The oil partially crystallized on being stored at ca. −20 °C. Dissolution of the material in the minimum volume of boiling 10:1 heptane–ethyl acetate gave a solution which deposited the crystalline isomer [containing less than 3 mol % of the liquid isomer (NMR)]: mp 78–80 °C; IR ($CDCl_3$) 1708–1690 cm^{-1}; NMR ($CDCl_3$, 200 MHz) 1.20 (s, 3 H), 1.54–2.04 (m, 6 H), 2.24–2.60 (m, 3 H), 2.84–3.16 (m, 2 H), 4.01 (dd, J = 10.5, 2.7 Hz, 1 H), 7.22–7.36 (m, 3 H), 7.50–7.62 (m, 2 H); exact mass *m/e* 312.0627 (calcd for $C_{15}H_{20}O_2{}^{80}Se$, *m/e* 312.0629). Anal. Calcd for $C_{15}H_{20}O_2Se$: C, 57.88; H, 6.48; O, 10.28. Found: C, 57.57; H, 6.53; O, 9.99.

The proportion of the crystalline isomer varied from run to run and sometimes it was nearly the exclusive product.

3-Ethylenyl-2-[1-hydroxy-2-(phenylseleno)ethyl]-2-methylcyclopentanone (2b). The reaction was carried out exactly as for the preparation of **1b** by using methyllithium (1.80 M, ether solution, 0.72 mL, 1.30 mmol), silyl enol ether **2a** (255 mg, 1.30 mmol) in ether (10 mL), zinc chloride (0.94 mL of a saturated ether solution, 0.65 mmol), and (phenylseleno)acetaldehyde (259 mg, 1.30 mmol) in ether (3 mL plus a 1-mL rinse). Flash chromatography over silica gel (5 × 20 cm) with 9:1 heptane–ethyl acetate gave **2b** as two apparently homogeneous (TLC, silica, 9:1 heptane–ethyl acetate) selenides with a combined weight of 352 mg (83%). The material of higher R_f (255 mg, 60%) was an oil: IR ($CDCl_3$) 1732 cm^{-1} (br); NMR ($CDCl_3$, 200 MHz) δ 0.95 (s, 3 H), 1.62–2.50 (m, 4 H), 2.90–3.32 (m, 4 H), 3.68 (dd, J = 10, 4 Hz, 1 H), 5.04–5.15 (m, 2 H), 5.71–5.92 (m, 1 H), 7.22–7.32 (m, 3 H), 7.44–7.58 (m, 2 H); ^{13}C NMR ($CDCl_3$, 50.32 MHz) δ 13.5, 24.9, 31.7, 38.0, 46.8, 54.6, 73.6, 116.9, 127.1, 129.1, 129.5, 132.7, 137.4, 222.3; exact mass *m/e* 324.0632 (calcd for $C_{16}H_{20}O_2{}^{80}Se$, *m/e* 324.0638). Anal. Calcd for $C_{16}H_{20}O_2Se$: C, 59.44; H, 6.24; O, 9.90. Found: C, 59.57; H, 6.25; O, 9.84.

The material of lower R_f (97.1 mg, 23%) solidified when stored at −20 °C: mp 88–89 °C (from 10:1 hexane–ethyl acetate);[42] IR ($CDCl_3$) 1738 cm^{-1}; NMR ($CDCl_3$, 200 MHz) δ 0.89 (s, 3 H), 1.48–2.48 (m, 4 H), 2.60–2.80 (br, s, 1 H), 2.93 (dd, J = 12.0, 12.8 Hz, 1 H), 3.12–3.28 (m, 2 H), 3.84 (br d, J = 12 Hz, 1 H), 5.08–5.26 (m, 2 H), 5.76–5.98 (m, 1 H), 7.16–7.32 (m, 3 H), 7.40–7.56 (m,

---

[36] Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43* 2923.

[37] Funk, R. L.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1980**, *102*, 5253. See also: Funk, R. L.; Vollhardt, K. P. C. *Synthesis* **1980**, 118.

[38] The integration of the Me_3Si signal was low due to saturation effects.

[39] House, H. O.; Latham, R. A.; Slater, C. D. *J. Org. Chem.* **1966**, *31*, 2667.

[40] Cf. ref 37 and 39.

[41] Stork, G.; Hudrlik, P. F. *J. Am. Chem. Soc.* **1968**, *90*, 4464.

[42] The material was dissolved in the minimum volume of the boiling *premixed* solvent.

2 H); ^{13}C NMR (CDCl$_3$, 50.32 MHz) δ 14.7, 25.6, 32.5, 38.0, 43.7, 55.1, 74.3, 116.9, 127.4, 129.3, 132.9, 138.8, 221.2; exact mass *m/e* 324.0628 (calcd for $C_{16}H_{20}O_2{}^{80}Se$, *m/e* 324.0630). Anal. Calcd for $C_{16}H_{20}O_2Se$: C, 59.44, H, 6.24; O, 9.90. Found: C, 59.45; H, 6.23; O, 9.97.

3-Ethenyl-2-[1-hydroxy-2-(phenylseleno)ethyl]cyclohexanone (3b). The reaction was carried out exactly as for the preparation of **1b** by using methyllithium (1.75 M, ether solution, 1.98 mL, 3.46 mmol), silyl enol ether **3a** (680 mg, 3.46 mmol) in ether (10 mL), zinc chloride (2.51 mL of a saturated ether solution, 1.73 mmol), and (phenylseleno)acetaldehyde (689 mg, 3.46 mmol) in ether (3 mL plus a 1-mL rinse). Flash chromatography over silica gel (5 × 15 cm) with 5:1 heptane–ethyl acetate gave **3b** as two apparently[43] homogeneous (TLC, silica, 5:1 heptane–ethyl acetate) selenides with a combined weight of 1.01 g (90%). The material of higher R_f (619 mg, 55%) was an oil: IR (CDCl$_3$) 1692 cm^{-1}; NMR (CDCl$_3$, 200 MHz) δ 1.45–2.34 (m, 6 H), 2.52–2.76 (m, 2 H), 3.10–3.45 (m, 3 H), 3.79 (br dd, *J* = 16.8, 9.7 Hz, 1 H), 4.93–5.18 (m, 2 H), 5.47–5.69 (m, 1 H), 7.15–7.39 (m, 3 H), 7.41–7.69 (m, 2 H); ^{13}C NMR (CDCl$_3$, 50.32 MHz) δ 26.2, 32.3, 32.7, 43.0, 47.3, 55.9, 70.3, 116.5, 127.1, 129.2, 129.6, 132.8, 139.9, 214.6; exact mass *m/e* 324.0628 (calcd for $C_{16}H_{20}O_2{}^{80}Se$, *m/e* 324.0628). Anal. Calcd for $C_{16}H_{20}O_2Se$: C, 59.44; H, 6.24; O, 9.90. Found: C, 59.62; H, 6.20; O, 9.78.

The material of lower R_f (393 mg, 35%) crystallized on storage at −20 °C; mp 46.5–47 °C (from 10:1 heptane–ethyl acetate);[43] IR (CDCl$_3$) 1697 cm^{-1}; NMR (CDCl$_3$, 200 MHz) δ 1.48–2.14 (m, 4 H), 2.16–2.58 (m, 3 H), 2.66 (br dd, *J* = 10, 5.2 Hz, 1 H), 2.88–3.46 (m, 3 H), 3.88–4.16 (m, 1 H), 4.90–5.06 (m, 2 H), 5.54–5.78 (m, 1 H), 7.18–7.40 (m, 3 H), 7.42–7.74 (m, 2 H); ^{13}C NMR (CDCl$_3$, 50.32 MHz) δ 24.6, 31.8, 32.6, 41.9, 45.3, 58.5, 69.9, 115.8, 127.1, 129.0, 133.2, 140.2, 212.8; exact mass *m/e* 324.0627 (calcd for $C_{16}H_{20}O_2{}^{80}Se$, *m/e* 324.0628). Anal. Calcd for $C_{16}H_{20}O_2Se$: C, 59.44; H, 6.24; O, 9.90. Found: C, 59.65; H, 6.16; O, 9.80.

2-[1-Hydroxy-2-(phenylseleno)ethyl]-3-(1-methylethenyl)cyclohexanone (4b). The reaction was carried out exactly as for the preparation of **1b** by using methyllithium (1.75 M, ether solution, 2.72 mL, 4.75 mmol), silyl enol ether **4a** (1.00 g, 4.75 mmol) in ether (11 mL), zinc chloride (3.45 mL of a saturated ether solution, 2.38 mmol), and (phenylseleno)acetaldehyde (946 mg, 4.75 mmol) in ether (4 mL plus a 2-mL rinse). Flash chromatography over silica gel (5 × 20 cm) with 5:1 heptane–ethyl acetate gave **4b** as two apparently homogeneous (TLC, silica, 5:1 heptane–ethyl acetate) selenides with a combined weight of 1.43 g (89%). The material of higher R_f (907 mg, 56%) crystallized on storage at −20 °C: mp 30–31 °C (from hexane); IR (neat) 1693 cm^{-1}; NMR (Me$_2$SO-d_6, 200 MHz) δ 1.44–1.96 (m, including a singlet broadened by unresolved coupling at δ 1.64, 7 H), 2.10–2.34 (m, 2 H), 2.54–2.74 (m, 2 H), 3.10–3.38 (m, 2 H), 3.73 (br q d, *J* = 6.7, 2.5 Hz, 1 H), 4.66–4.83 (m, 3 H), 7.18–7.38 (m, 3 H), 7.40–7.58 (m, 2 H); ^{13}C NMR (CDCl$_3$, 50.32 MHz) δ 18.2, 26.5, 31.1, 32.3, 43.1, 50.7, 53.9, 70.5, 113.5, 126.9, 129.2, 129.9, 132.3, 144.9, 215.6; exact mass *m/e* 338.0784 (calcd for $C_{17}H_{22}O_2{}^{80}Se$, *m/e* 338.0784). Anal. Calcd for $C_{17}H_{22}O_2Se$: C, 60.53; H, 6.57; O, 9.49. Found: C, 60.49; H, 6.60; O, 9.48.

The material of lower R_f (523 mg, 33%) also crystallized on storage at −20 °C; mp 40–41 °C (from hexane); IR (neat) 1697 cm^{-1}; NMR (CDCl$_3$, 200 MHz) δ 1.52–1.90 (m, including a singlet broadened by unresolved coupling at δ 1.70, 6 H), 1.92–2.12 (m, 1 H), 2.17–2.53 (m, 3 H), 2.83 (dd, *J* = 12, 4.8 Hz, 1 H), 2.96–3.43 (m, 3 H), 3.72–3.92 (m, 1 H), 4.68–4.78 (m, 2 H), 7.19–7.36 (m, 3 H), 7.46–7.62 (m, 2 H); ^{13}C NMR (CDCl$_3$, 50.32 MHz) δ 18.3, 24.9, 30.9, 32.2, 42.2, 49.0, 56.6, 70.0, 113.2, 127.0, 129.0, 130.0, 133.2, 145.0, 213.4; exact mass, *m/e* 338.0784 (calcd for $C_{17}H_{22}O_2{}^{80}Se$, *m/e* 338.0784). Anal. Calcd for $C_{17}H_{22}O_2Se$: C, 60.53; H, 6.57; O, 9.49. Found: C, 60.27; H, 6.52; O, 9.45.

2,5-Dimethyl-2-[1-hydroxy-2-(phenylseleno)ethyl]cyclohexanone (5b). Butyllithium (1.52 M, hexane solution, 2.48 mL, 3.77 mmol) was injected dropwise at −78 °C into a stirred solution of diisopropylamine (572 mg, 5.65 mmol) in ether (15 mL) containing a few milligrams of 2,2′-dipyridyl, and the solution was kept for 30 min. 2,6-Dimethylcyclohexanone (as a mixture of isomers, 480 mg, 3.78 mmol) in ether (6 mL plus a 2-mL rinse) was added over 15 min. Stirring was continued for 30 min, and the mixture was then allowed to warm to 0 °C over about 30 min. Zinc chloride (2.73 mL of a saturated ether solution, 1.88 mmol) was added dropwise. Stirring at 0 °C was continued for 10 min, and (phenylseleno)acetaldehyde (787 mg, 3.96 mmol) in ether (4 mL plus 2 mL rinse) was injected rapidly (main portion added over ca. 3 s). The mixture was stirred 5 min and worked up as for **1b**. Flash chromatography over silica gel (5 × 15 cm) with 4:1 heptane–ethyl acetate gave **5b** (1.10 g, 89%) as a mixture of diastereoisomers that were partially resolvable by TLC (silica, 4:1 heptane–ethyl acetate): IR (neat) 1703 cm^{-1}; NMR (CDCl$_3$, 200 MHz) δ 0.85–1.09 (m, 6 H), 1.15–2.1 (m, 6 H), 2.48–3.3 (m, 4 H), 4–4.2 (m, 1 H), 7.2–7.38 (m, 3 H), 7.45–7.62 (m, 2 H); ^{13}C NMR (CDCl$_3$, 100.61 MHz) δ 15.1, 17.1, 20.7, 32.5, 36.0, 37.7, 41.6, 52.7, 72.6, 127.7, 129.4, 133.4, 214.5. Signals due to a minor isomer were present at δ 15.0, 16.7, 20.3, 33.2, 35.9, 36.7, 42.8, 70.9, 133.7; exact mass, *m/e* 326.0786 (calcd for $C_{16}H_{22}O_2{}^{80}Se$, *m/e* 326.0785). Anal. Calcd for $C_{16}H_{22}O_2Se$: C, 59.08; H, 6.82; O, 9.84. Found: C, 59.02; H, 6.78; O, 9.56.

2-[1-Hydroxy-2-(phenylseleno)ethyl]-2,5,5-trimethylcyclohexanone (6b). Butyllithium (1.54 M, hexane solution, 2.45 mL, 3.77 mmol) was injected dropwise at −78 °C into a stirred solution of diisopropylamine (572 mg, 5.65 mmol) in ether (15 mL) containing a few milligrams of 2,2′-dipyridyl. The solution was kept for 30 min, warmed to −30 °C, and stirred for 30 min. 2,2,6-Trimethylcyclohexanone (528 mg, 3.77 mmol) in ether (6 mL plus a 2-mL rinse) was added over 15 min. The reaction mixture was kept at −30 °C for 1.25 h and was then warmed to 0 °C over 30 min. Zinc chloride (2.73 mL of a saturated ether solution, 1.88 mmol) was added dropwise, and stirring at 0 °C was continued for 5 min. (Phenylseleno)acetaldehyde (750 mg, 3.77 mmol) in ether (4 mL plus a 2-mL rinse) was injected rapidly (main portion added over ca. 3 s). The mixture was stirred 5 min and worked up as for **1b**. Flash chromatography over silica gel (5 × 15 cm) with 4:1 heptane–ethyl acetate gave **6b** (966 mg, 75%) as a mixture [73:27 (NMR)] of diastereoisomers that were not resolved by TLC (silica, 4:1 heptane–ethyl acetate): IR (neat) 1689 cm^{-1}; NMR (CDCl$_3$, 200 MHz) δ 1.03 (s, 0.8 H), 1.07 (s, 2.2 H), 1.11 (s, 0.8 H), 1.13 (s, 0.8 H), 1.15 (s, 2.2 H), 1.22 (s, 2.2 H), 1.42–2.14 (m, 6 H), 2.72–2.95 (m, 0.5 H), 2.96–3.14 (m, 1.5 H), 3.56–3.78 (br s, 1 H), 3.83–4.06 (m, 1 H), 7.17–7.34 (m, 3 H), 7.43–7.60 (m, 2 H); exact mass, *m/e* 340.0933 (calcd for $C_{17}H_{24}O_2{}^{80}Se$, *m/e* 340.0942). Anal. Calcd for $C_{17}H_{24}O_2Se$: C, 60.17; H, 7.13; O, 9.43. Found: C, 60.19; H, 7.18; O, 9.34.

2-[1-Hydroxy-2-(phenylseleno)ethyl]cyclohexanone (7b). LDA was prepared as in the synthesis of **6b** by using butyllithium (1.52 M, hexane solution, 3.74 mL, 5.68 mmol) and diisopropylamine (864 mg, 8.54 mmol) in ether (18 mL) containing a few milligrams of 2,2′-dipyridyl. The solution was warmed to −20 °C over 30 min, and cyclohexanone (560 mg, 5.70 mmol) in ether (10 mL plus a 4-mL rinse) was injected over 15 min. Chlorodibutylborane[44] (915 mg, 5.70 mmol) in ether (14 mL plus a 7-mL rinse) was added over 3 min, and the solution was stirred for 1 h. (Phenylseleno)acetaldehyde (1.13 g, 5.69 mmol) in ether (18 mL plus a 6-mL rinse) was added at −30 °C at a fast dropwise rate, and stirring at −30 °C was continued for 2 h. The mixture was then cooled to −78 °C, and trimethylamine *N*-oxide[23] (1.28 g, 17.1 mmol) in methanol (27 mL) was injected dropwise. The cold bath was removed, and stirring was continued overnight. The mixture was evaporated, and flash chromatography (twice) over silica gel (5 × 15 cm) with 5:1 heptane–ethyl acetate gave **7b** (1.33 g, 78%) as an apparently homogeneous[45] (TLC, silica, 5:1 heptane–ethyl acetate) oil: IR (neat) 1704 cm^{-1}; NMR (CDCl$_3$, 200 MHz) δ 1.38–2.47 (m, 9 H), 2.49–2.79 (m, 1 H), 2.97–3.35 (m, 2 H), 3.85–4.01 (m, 0.6 H), 4.13–4.28 (m, 0.4 H), 7.21–7.39 (m, 3 H), 7.47–7.67 (m, 2 H); exact mass, *m/e* 298.0481 (calcd for $C_{14}H_{18}O_2{}^{80}Se$, *m/e* 298.0472). Anal. Calcd for $C_{14}H_{18}O_2Se$: C, 56.57; H, 6.10; O, 10.76. Found: C, 56.80; H, 6.26; O, 10.61.

3-Ethenyl-2-[1-hydroxy-2-(phenylseleno)ethyl]cyclooctanone (8b). Anhydrous copper(I) iodide (3.85 g, 16.2 mmol) was added from a side-arm addition tube to a magnetically stirred

---

[43] The ^{13}C NMR spectrum of the low-R_f material showed the presence of ca. 5.5% of another component.

[44] Brown, H. C. "Organic Synthesis via Boranes"; Wiley: New York, 1975. See also: Brown, H. C.; Ravindran, N. *J. Am. Chem. Soc.* **1972**, *94*, 2112.

[45] The ^{1}H NMR spectrum shows the presence of two isomers.

solution of vinylmagnesium bromide (1.28 M, THF solution, 25.3 mL, 32.4 mmol) at -5 °C. The ice bath was immediately replaced by an acetone–dry ice bath at -45 °C. Cyclooctenone[46] (2.01 g, 16.2 mmol) in ether (2.5 mL plus a 0.5-mL rinse) was injected dropwise over 2 min, and the mixture was kept 2 h at -45 °C. It was then brought to ice-bath temperature (over about 10 min), and (phenylseleno)acetaldehyde (3.21 g, 16.2 mmol) in ether (12 mL plus a 1-mL rinse) was injected rapidly (main fraction added over ca. 10 s). Stirring was continued for 5 min, and the mixture was partitioned between saturated aqueous ammonium chloride (150 mL) and ether (1 × 150, 2 × 25 mL). The combined organic extract was washed with brine, dried, and evaporated. Flash chromatograhy over silica gel (5 × 25 cm) with 4:1 hexane–ethyl acetate gave an oily liquid (1.84 g), and crystallization from hexane afforded **8b**: 1.42 g (25%); mp 58–59 °C. The mother liquors and the mixed fractions from the flash chromatography were evaporated, and flash chromatography (5 × 20 cm) using the above system followed by crystallization provided a further crop (523 mg, 9%) of **8b**: mp 58.5–59 °C; IR (CCl_4) 1705 cm^{-1}; NMR ($CDCl_3$, 200 MHz) δ 1.18–1.90 (m, 7 H), 1.94–2.59 (m, 4 H), 2.60–3.00 (br s, 1 H), 3.16–3.40 (m, 3 H), 3.70–3.86 (m, 1 H), 4.80–5.06 (m, 2 H), 5.48–5.74 (m, 1 H), 7.16–7.34 (m, 3 H), 7.40–7.56 (m, 2 H); ^{13}C NMR ($CDCl_3$, 50.32 MHz) δ 22.8, 23.2, 28.5, 32.5, 33.4, 46.1, 46.6, 54.5, 71.3, 115.3, 127.3, 129.0, 133.3, 140.9, 218.3; exact mass, *m/e* 352.0936 (calcd for $C_{18}H_{24}O_2{}^{80}Se$, *m/e* 352.0941). Anal. Calcd for $C_{18}H_{24}O_2Se$: C, 61.53; H, 6.89; O, 9.11. Found: C, 61.35; H, 6.85; O, 8.96.

2-[1-Hydroxy-2-(phenylseleno)ethyl]cyclodecanone (9b). Apart from the fact that the cyclodecanone was added over 1.5 h (as opposed to 15 min) the procedure for **6b** was followed by using butyllithium (1.40 M, hexane solution, 3.47 mL, 4.86 mmol), diisopropylamine (492, 4.86 mmol) in ether (13 mL), cyclodecanone (750.0 mg, 4.86 mmol) in ether (6 mL plus a 3-mL rinse), zinc chloride (3.52 mL of a saturated ether solution, 2.43 mmol), and (phenylseleno)acetaldehyde (968 mg, 4.86 mmol) in ether (4 mL plus a 1-mL rinse). Flash chromatography over silica gel (5 × 15 cm) with 4:1 heptane–ethyl acetate gave **9b** (1.68 g, 85%) as a homogeneous (TLC, silica, 4:1 heptane–ethyl acetate) oil which solidified on standing and was recrystallized from hexane: mp 44.5–45.5 °C; IR (neat) 1697 cm^{-1}; NMR ($CDCl_3$, 200 MHz) δ 1.06–1.96 (m, 14 H), 2.24–2.50 (m, 1 H), 2.63–2.83 (m, 1 H), 2.84–3.24 (m, 4 H), 3.63–3.84 (m, 1 H), 7.23–7.42 (m, 3 H), 7.45–7.62 (m, 2 H); ^{13}C NMR ($CDCl_3$, 100.61 MHz) δ 23.3, 24.3, 24.4, 25.3, 25.4, 25.5, 26.3, 33.3, 43.9, 56.2, 71.5, 127.4, 129.3, 133.0, 133.2, 216.9; exact mass, *m/e* 354.1098 (calcd for $C_{18}H_{26}O_2{}^{80}Se$, *m/e* 354.1098). Anal. Calcd for $C_{18}H_{26}O_2Se$: C, 61.18; H, 7.42; O, 9.06. Found: C, 61.28; H, 7.50; O, 9.23.

2-[1-Hydroxy-1-methyl-2-(phenylseleno)ethyl]cyclohexanone (10b). LDA was prepared as described for **6b** from butyllithium (0.99 M, hexane solution, 5.15 mL, 5.10 mmol) and diisopropylamine (772 mg, 7.63 mmol) in ether (15 mL) containing a few milligrams of 2,2′-dipyridyl. The solution was kept at -78 °C for 30 min and then warmed to -30 °C over 30 min. Cyclohexanone (500 mg, 5.10 mmol) in ether (8 mL plus a 2-mL rinse) was added over 10 min. The mixture was stirred for 20 min and then allowed to warm to 0 °C over 15 min. Zinc chloride (3.69 mL of a saturated solution, 2.55 mmol) was added, stirring was continued for 5 min, and (phenylseleno)acetone[27] (1.09 g, 5.10 mmol) in ether (6 mL plus a 2-mL rinse) was injected rapidly (main portion added over ca. 6 s). The mixture was stirred for 30 min at 0 °C and then worked up as for **1b**. Flash chromatography over silica (5 × 15 cm) with 10:1 heptane–ethyl acetate gave **10b** (1.06 g, 67%) as a mixture (NMR) of two diastereoisomers that were partially resolvable by TLC (silica, 10:1 heptane–ethyl acetate): IR (neat) 1692 cm^{-1}; NMR ($CDCl_3$, 200 MHz) δ 1.29 (s, 1.7 H), 1.36 s, 1.3 H), 1.39–2.4 (m, 8 H), 2.55–2.72 (m, 0.44 H), 2.77–2.94 (m, 0.50 H), 3.0–3.55 (series of sharp singlets, 2.46 H), 4.18 (s, 0.51 H), 7.18–7.35 (m, 3 H), 7.45–7.7 (m, 2 H); ^{13}C NMR ($CDCl_3$, 50.23 MHz) δ 24.5, 24.8, 25.1, 25.4, 27.9, 28.2, 29.5, 29.6, 39.9, 43.2, 43.4, 56.3, 58.5, 73.8, 126.9, 129.1, 129.5, 132.7, 132.9, 214.0, 216.1; exact mass, *m/e* 312.0631 (calcd for $C_{15}H_{20}O_2{}^{80}Se$, *m/e* 312.0629). Anal. Calcd for $C_{15}H_{20}O_2Se$: C, 57.88; H, 6.48; O, 10.28. Found: C, 57.88; H, 6.48; O, 10.31.

2-Ethenyl-2-methylcyclohexanone (1c).[47] **Method A.** Triethylamine (2.17 mL, 15.6 mmol) was injected into a stirred solution of **1b** [crystalline (low R_f) material; 941 mg, 3.02 mmol] in dichloromethane (25 mL). Methanesulfonyl chloride (1.09 g, 9.49 mmol) in dichloromethane (9 mL plus a 1-mL rinse) was injected over 1.5 h. The mixture was stirred for a further arbitrary period of 10 min and then poured into dichloromethane (50 mL). The mixture was washed with ice-cold hydrochloric acid (0.1 N, 50 mL), with saturated sodium hydrogen carbonate (50 mL), and finally with brine (50 mL). It was dried and evaporated, and the residue was distilled twice in a Kugelrohr apparatus [bp 83 °C (3 mm)] to give **1c** (344 mg, 82%) as a homogeneous (VPC) oil: IR (neat) 1713 cm^{-1}; NMR ($CDCl_3$, 200 MHz) δ 1.19 (s, 3 H), 1.53–2.07 (m, 6 H), 2.26–2.63 (m, 2 H), 4.95–5.20 (m, 2 H), 6.01 (dd, J = 18.4, 12 Hz, 1 H). For analysis the ketone (from a different experiment) was converted into its 2,4-dinitrophenylhydrazone (64% based on **1b**): mp 157–158 °C (from 95% ethanol); exact mass, *m/e* 318.1325 (calcd for $C_{15}H_{18}N_4O_4$, *m/e* 318.1328). Anal. Calcd for $C_{15}H_{18}N_4O_4$: C, 56.60; H, 5.70; N, 17.60. Found: C, 56.48; H, 5.63; N, 17.77.

Method B. Use of Phosgene. Pyridine (0.11 mL, 1.36 mmol) was added to the hydroxy selenide **1b** [crystalline (low R_f) material; 209 mg, 0.671 mmol] in ether (10 mL). The solution was cooled to -78 °C, and phosgene (ca. 80 drops) was condensed into it. The flask was then closed with a septum, and an exit needle, attached to a bubbler, was passed through the septum. The mixture was stirred for 18 h, during which period the cold bath attained room temperature. The solvent was removed under water-pump vacuum (protection from moisture) and replaced by dry acetonitrile (10 mL). Anhydrous sodium iodide (403 mg, 2.69 mmol) was added, the mixture was stirred for 18 h, and the solvent was evaporated. The residue was stirred with ether (50 mL), and the flask was rinsed with 10% w/v aqueous sodium hydrogen sulfite (5 mL) and with ether (10 mL). These extracts were mixed, and the ether layer was separated and washed with 10% w/v aqueous sodium hydrogen sulfite (50 mL), saturated sodium hydrogen carbonate (50 mL), and brine (50 mL). It was dried and evaporated. The NMR spectrum (200 MHz) of the residue showed the presence of **1c** (78%, using an internal standard).

2,3-Diethenyl-2-methylcyclopentanone (2c). From High-R_f Hydroxy Selenide. The procedure for **1c** was followed by using triethylamine (0.49 mL, 3.54 mmol), **2b** (high-R_f material, 220 mg, 0.679 mmol) in dichloromethane (8 mL), methanesulfonyl chloride (246 mg, 2.15 mmol) in dichloromethane (4 mL plus a 1-mL rinse, added over 1.5 h), and an arbitrary reaction period of 1 h. The acid wash used in the isolation of **1c** was omitted from the workup. Kugelrohr distillation [twice, bp 93 °C (3 mm)] gave **2c** (83.8 mg, 82%) as an oil containing ca. 3% of an impurity (VPC) judged by VPC–mass spectral analysis to be an isomer (presumably a geometric isomer): IR ($CDCl_3$) 1735 cm^{-1}; NMR ($CDCl_3$, 200 MHz) δ 1.00 (s, 3 H), 1.73–1.97 (m, 1 H), 2.05–2.57 (m, 3 H), 2.71–2.88 (m, 1 H), 5.07–5.26 (m, 4 H), 5.70–5.92 (m, 2 H); ^{13}C NMR ($CDCl_3$, 50.32 MHz) δ 16.2, 24.3, 36.5, 49.7, 115.3, 116.6, 136.6, 140.3; exact mass, *m/e* 150.1040 (calcd for $C_{10}H_{14}O$, *m/e* 150.1045). Anal. Calcd for $C_{10}H_{14}O$: C, 79.96; H, 9.39. Found: C, 80.15; H, 9.40.

From Low-R_f Hydroxy Selenide. The procedure for **1c** was followed by using triethylamine (0.21 mL, 1.47 mmol), **2b** (low-R_f material, 91.1 mg, 0.282 mmol) in dichloromethane (2.5 mL), methanesulfonyl chloride (102 mg, 0.891 mmol) in dichloromethane (2.5 mL plus a 0.5-mL rinse, added over 1.5 h), and an arbitrary reaction period of 10 min. The mixture was poured into 2:1 pentane–ether (75 mL) and washed with 2% w/w ice-cold hydrochloric acid (50 mL), with saturated sodium hydrogen carbonate (50 mL), and finally with brine (50 mL). The organic phase was dried and evaporated. Kugelrohr distillation [twice, bp 92 °C (3 mm)] gave **2c** (35.7 mg, 84%) as a homogeneous (TLC, silica, 5:1 heptane–ethyl acetate, or silica impregnated with 5% w/w silver nitrate, ethyl acetate) oil that was better than 99% pure by VPC: IR (neat) 1742 cm^{-1}; exact mass, *m/e* 150.1043 (calcd for $C_{10}H_{14}O$, *m/e* 150.1044). The NMR spectrum (200 MHz) was identical with that of material obtained from the high-R_f hydroxy selenide.

***trans*-2,3-Diethenylcyclohexanone (3c). From High-R_f**

---

[46] Garbisch, E. W., Jr. *J. Org. Chem.* **1965**, *30*, 2109.

[47] Marvell, E. N.; Rusay, R. *J. Org. Chem.* **1977**, *42*, 3336.

Hydroxy Selenide. The procedure for **2c** (low R_f) was followed by using triethylamine (0.22 mL, 1.60 mmol), **3b** (high-R_f material, 100 mg, 0.308 mmol) in dichloromethane (5 mL), methanesulfonyl chloride (112 mg, 0.974 mmol) in dichloromethane (4 mL plus a 1-mL rinse, added over 1.5 h), and an arbitrary reaction period of 1 h. The acid wash used in the isolation of **2c** (low R_f) was omitted from the workup. After evaporation of the organic extract, the residue was filtered through silica (2 × 3.5 cm) with 4:1 hexane–ethyl acetate. Kugelrohr distillation [50 °C (0.01 mm)] then gave **3c** (38 mg, 82%) as an apparently homogeneous (TLC, silica, 4:1 heptane–ethyl acetate) oil. VPC–mass spectral analysis of the mixture revealed two components: **3c** and an isomer (probably the 2,3-cis isomer) in the ratio of 39:1.[48] For **3c**: IR (neat) 1712 cm^{-1}; NMR (CDCl$_3$, 200 MHz) δ 1.54–2.25 (m, 4 H), 2.25–2.58 (m, 3 H), 2.87 (dd, J = 10.7, 8.5 Hz, 1 H), 4.92–5.13 (m, 3 H), 5.22–5.34 (m, 1 H), 5.64–5.90 (m, 2 H); ^{13}C NMR (CDCl$_3$, 15.08 MHz) δ 25.6, 31.1, 41.5, 48.4, 60.4, 115.0, 118.6, 134.9, 140.7, 210.6; exact mass, m/e 150.1045 (calcd for $C_{10}H_{14}O$, m/e 150.1044). Anal. Calcd for $C_{10}H_{14}O$: C, 79.96; H, 9.39. Found: C, 79.77; H, 9.49.

From Low-R_f Hydroxy Selenide. The procedure for **2c** (low R_f) was followed by using triethylamine (0.41 mL, 2.96 mmol), **3b** (low-R_f material, 184 mg, 0.569 mmol) in dichloromethane (5 mL), methanesulfonyl chloride (206 mg, 1.80 mmol) in dichloromethane (4 mL plus a 1-mL rinse, added over 1.5 h), and an arbitrary reaction period of 10 min. After evaporation of the organic extract following the workup as described for **2c** (low R_f), the residue was chromatographed over silica with 5:1 heptane–ethyl acetate, but this process did not remove all impurities. The material, which contained no conjugated ketone (IR control), was distilled in a Kugelrohr apparatus [bp 60 °C (0.3 mm)] to give the product (60.7 mg, 71%). VPC–mass spectral analysis revealed three isomeric components: **3c**, probably its 2,3-cis isomer, and 3-ethenyl-2-ethylidenecyclohexanone in the ratio of 9.3:1:7.4.[48,49] The mixture had IR (neat) absorbances at 1712 and 1689 cm^{-1}. The NMR spectrum (CDCl$_3$, 200 MHz) showed inter alia signals at δ 2.87 (dd, J = 10.7, 8.5 Hz) and 6.89 (dq, J = 7.5, 1.6 Hz) with areas in a ratio of 1.05:1.

***trans*-2-Ethenyl-3-(1-methylethenyl)cyclohexanone (4c).**[4a] **From High-R_f Hydroxy Selenide.** The procedure for **1c** was followed by using triethylamine (0.34 mL, 2.43 mmol), **4b** (high-R_f material, 162 mg, 0.480 mmol) in dichloromethane (5 mL), methanesulfonyl chloride (165 mg, 1.44 mmol) in dichloromethane (4 mL plus a 1-mL rinse, added over 1.5 h), and an arbitrary reaction period of 10 min. After the workup specified for **1c**, the product was distilled twice in a Kugelrohr apparatus [bp 82 °C (0.1 mm)] to yield **4c** (70.7 mg, 89%) as a homogeneous (TLC, silica, 4:1 heptane–ethyl acetate) oil, better than 99% pure (VPC): IR (neat) 1711 cm^{-1}; NMR (CDCl$_3$, 200 MHz) δ 1.62–1.94 (m, including a singlet broadened by unresolved coupling at δ 1.70, 6 H), 2.00–2.20 (m, 1 H), 2.26–2.57 (m, 3 H), 3.01 (dd, J = 11.4, 8.8 Hz, 1 H), 4.69–4.82 (m, 2 H), 4.90–5.24 (m, 2 H), 5.59–5.82 (m, 1 H); exact mass, m/e 164.1196 (calcd for $C_{11}H_{16}O$, m/e 164.1201. Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.82. Found: C, 80.30; H, 9.83.

From Low-R_f Hydroxy Selenide. The procedure for **2c** (low R_f) was followed by using triethylamine (0.47 mL, 3.35 mmol), **4b** (low-R_f material, 227 mg, 0.671 mmol) in dichloromethane (5 mL), methanesulfonyl chloride (231 mg, 2.01 mmol) in dichloromethane (4 mL plus a 1-mL rinse, added over 1.5 h), and an arbitrary reaction period of 10 min. After the workup specified for **2c** (low R_f), Kugelrohr distillation [twice, bp 55 °C (0.01 mm)], column chromatography over silica (1 × 15 cm) with 5:1 hexane–ethyl acetate, and redistillation in a Kugelrohr apparatus gave **4c** (89 mg, 80%) as a colorless, homogeneous (TLC, silica, 5:1 heptane–ethyl acetate, or silica impregnated with 5% w/w silver nitrate, ethyl acetate) oil that was better than 98% pure by VPC and was spectroscopically identical with material from the high-R_f hydroxyselenide.

2,6-Dimethyl-2-ethenylcyclohexanone (5c). The procedure for **1c** was followed by using triethylamine (0.68 mL, 4.85 mmol), **5b** (a mixture of diastereomers, 304 mg, 0.933 mmol) in dichloromethane (10 mL), methanesulfonyl chloride (338 mg, 2.95 mmol) in dichloromethane (4 mL plus a 1-mL rinse, added over 1.5 h), and an arbitrary reaction period of 10 min. After the workup specified for **1c**, Kugelrohr distillation [twice, bp 90 °C (3.0 mm)] afforded **5c** (108 mg, 75%) that was better than 98% pure (VPC). The sample consisted of two isomers (VPC–mass spectral analysis) in the ratio of 34.5:1 (VPC): IR (neat) 1710 cm^{-1}; NMR (CDCl$_3$, 200 MHz) δ 1.00 (d, J = 7.1 Hz, 3 H), 1.15 (s, 3 H), 1.20–2.15 (m, 7 H), 2.61–2.83 (m, 1 H), 4.93–5.21 (m, 2 H), 5.91–6.09 (m, 1 H); ^{13}C NMR (CDCl$_3$, 50.32 MHz) δ 14.9, 22.0, 24.5, 37.0, 40.9, 42.1, 52.4, 115.2, 142.9, 214.3; exact mass, m/e 152.1195 (calcd for $C_{10}H_{16}O$, m/e 152.1201. Anal. Calcd for $C_{10}H_{16}O$: C, 78.90; H, 10.59. Found: C, 78.90; H, 10.55.

2-Ethenyl-2,6,6-trimethylcyclohexanone (6c). Method A. The procedure for **1c** was followed by using triethylamine (0.78 mL, 5.60 mmol), **6b** (mixture of diastereomers, 364 mg, 1.07 mmol) in dichloromethane (10 mL), methanesulfonyl chloride (389 mg, 3.39 mmol) in dichloromethane (4 mL plus a 1-mL rinse, added over 1.5 h), and an arbitrary reaction period of 10 min. After the workup specified for **1c**, Kugelrohr distillation [twice, bp 93 °C (3.2 mm)] gave **6c** (151 mg, 84%) as a homogeneous (TLC, silica, 4:1 heptane–ethyl acetate) oil that was better than 99% pure (VPC): IR (neat) 1700 cm^{-1}; NMR (CDCl$_3$, 200 MHz) δ 1.10 (s, 3 H), 1.12 (s, 3 H), 1.16 (s, 3 H), 1.52–2.18 (m, 6 H), 5.05–5.18 (m, 2 H), 5.84–6.02 (m, 1 H); ^{13}C NMR (CDCl$_3$, 50.32 MHz) δ 18.0, 26.8, 27.4, 27.8, 37.4, 40.1, 45.2, 50.9, 113.5, 142.9, 217.1; exact mass, m/e 166.1356 (calcd for $C_{11}H_{18}O$, m/e 166.1357). Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.91. Found: C, 79.31; H, 11.09.

Method B. Use of Phosgene. The procedure for **1c** was followed by using pyridine (0.075 mL, 0.927 mmol), **6b** (mixture of isomers, 158 mg, 0.466 mmol) in ether (10 mL), phosgene (ca. 80 drops), and sodium iodide (279 mg, 1.86 mmol) in acetonitrile (10 mL). Thirty minutes after addition of the sodium iodide a condenser was fitted to the flask (under a stream of nitrogen). The mixture was refluxed for 45 min, cooled, evaporated, and worked up in the specified manner. The NMR spectrum (200 MHz) of the residue showed the presence of **6c** (98%, using an internal standard).

2-Ethenylcyclohexanone (7c).[47] The procedure for **1c** was followed by using triethylamine (0.20 mL, 1.44 mmol), **7b** (a mixture of diastereomers, 87 mg, 0.293 mmol) in dichloromethane (2.5 mL), methanesulfonyl chloride (101 mg, 0.878 mmol) in dichloromethane (2 mL plus a 0.5-mL rinse, added over 1.5 h), and an arbitrary reaction period of 10 min. After the workup specified for **1c**, the combined organic extract was dried and evaporated (good water-pump vacuum) to afford **7c** [53.6% by NMR (200 MHz) with *p*-iodonitrobenzene as an internal standard]. We found compound **7c** to be very prone to isomerization.

***trans*-2,3-Diethenylcyclooctanone (8c).** Triethylamine (1.858 g, 22.5 mmol) was injected into a stirred solution of **8b** (1.569 g, 4.47 mmol) in dichloromethane (20 mL). The mixture was cooled in an ice bath and methanesulfonyl chloride (1.547 g, 13.5 mmol) in dichloromethane (13 mL plus a 2-mL rinse) was injected over 1.5 h. The ice bath was removed, and after 20 min (TLC control) the solution was shaken with a mixture of pentane (75 mL), ether (75 mL), and water (25 mL). The organic phase was washed with ice-cold 2% w/w hydrochloric acid, with saturated sodium hydrogen carbonate and with brine. The extract was dried (Na_2SO_4) and evaporated. Flash chromatography of the residue over silica gel (20 × 5 cm) with 3% v/v ethyl acetate–hexane gave material which was distilled in a Kugelrohr apparatus [64 °C (0.1 mm)]. Redistillation gave **8c** (517 mg, 68%) as an oil, homogeneous by TLC (silica, 5% w/w ethyl acetate–hexane) but of 97% purity by VPC: IR (CCl$_4$) 1701 cm^{-1}; NMR (CDCl$_3$, 200 MHz) δ 1.32–2.22 (m, 8 H), 2.30–2.70 (m, 3 H), 3.20 (dd, J = 11.3, 9.2 Hz, 1 H), 4.93–5.20 (m, 4 H), 5.47–5.90 (m, 2 H); ^{13}C NMR (CDCl$_3$, 100.61 MHz) δ 23.4, 24.9, 27.7, 33.0, 42.3, 46.6, 59.7, 114.8, 117.1, 136.9, 141.1, 215.4; exact mass, m/e 178.1356 (calcd for $C_{12}H_{18}O$, m/e 178.1358. Anal. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18; O, 9.10. Found: C, 80.54; H, 10.17; O, 8.91.

2-Ethenylcyclodecanone (9c). The procedure for **2c** (low R_f) was followed by using triethylamine (0.33 mL, 2.36 mmol), **9b** (165 mg, 0.467 mmol) in dichloromethane (5 mL), methanesulfonyl chloride (161 mg, 1.41 mmol) in dichloromethane (4 mL plus a 1-mL rinse, added over 1.5 h), and an arbitrary reaction period of 10 min. After the workup specified for **2c** (low R_f) the sample

---

(48) These are relative peak areas.

(49) Evidently extensive isomerization had occurred during distillation.

was subjected to flash chromatography over silica (2 × 20 cm) by using 30:1 hexane–ethyl acetate. The solvent was removed under vacuum at 20 °C, and the residue was distilled in a Kugelrohr apparatus [50 °C (0.01 mm)] to give **9c** (42 mg, 50%) as a homogeneous (TLC, silica, 4:1 hexane–ethyl acetate) oil which was pure by VPC: IR (neat) 1709 cm^{-1}; NMR ($CDCl_3$, 100 MHz) δ 1.00–2.38 (m, 14 H), 2.40–2.81 (m, 2 H), 3.38–3.73 (br td, J = 9, 2 Hz, 1 H), 4.88–5.30 (m, 2 H), 5.48–5.91 (m, 1 H); exact mass, m/e 180.1526 (calcd for $C_{12}H_{20}O$, m/e 180.1515). Anal. Calcd for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 80.10; H, 11.31.

When the progress of the experiment was monitored by NMR (200 MHz, internal standard) the yield of **9c** was found to be ca. 91% but the compound is very sensitive to rearrangement (to the conjugated isomer). Workup and chromatography at ca. 0 °C did not improve the yield.

2-(1-Methylethenyl)cyclohexanone (10c).[50] The procedure for **1c** was followed by using triethylamine (0.55 mL, 3.97 mmol), **10b** (mixture of diastereomers, 247 mg, 0.795 mmol) in dichloromethane (10 mL), methanesulfonyl chloride (273 mg, 2.38 mmol) in dichloromethane (2.5 mL plus a 0.5-mL rinse, added over 1.5 h), and an arbitrary reaction period of 0.5 h. The acid wash used for the isolation of **1c** was omitted from the workup. The combined organic extract was dried and evaporated (good water pump vacuum) to afford **10c** [62% by NMR (200 MHz), using *p*-iodonitrobenzene as an internal standard; 91% after correction for starting material[51] (78.3 mg, 31%) recovered by flash chromatography of the NMR sample over silica (2 × 15 cm) with 4:1 heptane–ethyl acetate].

For characterization of **10c** the experiment was repeated on almost the same scale, and the reaction mixture was poured into pentane–ether and washed as described for **4c** (low R_f). The organic phase was dried and evaporated, and the residue was chromatographed over silica impregnated with 5% w/w silver nitrate (1 × 35 cm) by using 5:1 hexane–ethyl acetate. Kugelrohr distillation [bp 30 °C (0.01 mm)] then afforded **10c** as a homogeneous (TLC, silica impregnated with 5% w/w silver nitrate, 5:1 hexane–ethyl acetate) oil: IR (neat) 1710 cm^{-1}; NMR ($CDCl_3$, 200 MHz) δ 1.54–2.20 (m, including a singlet broadened by unresolved coupling at δ 1.77, 9 H), 2.24–2.54 (m, 2 H), 3.04 (dd, J = 11.3, 5.4 Hz, 1 H), 4.70–4.82 (m, 1 H), 4.90–5.03 (m, 1 H); exact mass, m/e 138.1046 (calcd for $C_9H_{14}O$, m/e 138.1045). Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.12; H, 10.16.

1,2-Diethenyl-2-methylcyclohexanol (1d and 1d′). Vinylmagnesium bromide (0.92 M in THF, 6.10 mL, 5.61 mmol) was injected over ca. 2 min into a stirred solution, kept at −30 °C, of **1c** (380 mg, 2.75 mmol) in THF (10 mL). The cold bath was then removed, and, after an arbitrary period of 30 min, the reaction mixture was partitioned between 2:1 pentane–ether (75 mL) and ice-cold hydrochloric acid (2% w/w, 50 mL). The aqueous layer was extracted with ether (25 mL), and the combined organic phase was washed with saturated aqueous sodium hydrogen carbonate (50 mL) and with brine and was then dried. Evaporation of the extract and Kugelrohr distillation [bp 94 °C (3 mm)] gave the product (320 mg, 70%) as a mixture of isomers. Chromatography over silica impregnated with 5% w/w silver nitrate (2 × 70 cm) with 1:4 hexane–ethyl acetate afforded 51 mg of low-R_f material. The other isomer from the silica silver nitrate column was rechromatographed over silica (1 × 25 cm) by using 1:8 ethyl acetate–hexane to yield 170 mg of high-R_f product.

1d (low-R_f compound): IR (neat) 3470, 3080, 3020, 1634 cm^{-1}; NMR ($CDCl_3$, 200 MHz) δ 1.08 (s, 3 H), 1.18–1.34 (m, 1 H), 1.36–2.01 (m, 8 H), 4.97–5.33 (m, 4 H), 5.89–6.16 (m, 2 H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 21.1, 21.3, 21.8, 32.0, 33.4, 43.2, 75.0, 113.1, 114.5, 142.5, 144.8; exact mass, m/e 166.1356 (calcd for $C_{11}H_{18}O$, m/e 166.1358). Anal. Calcd for $C_{11}H_{18}O$: C, 79.47; H, 10.91. Found: C, 79.47; H, 10.85.

1d′ (high-R_f compound): IR (neat) 3480, 3080, 3020, 1633 cm^{-1}; NMR ($CDCl_3$, 200 MHz) δ 1.03 (s, 3 H), 1.35–1.80 (m, 9 H), 4.96–5.33 (m, 4 H), 6.03–6.25 (m, 2 H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 20.1, 21.2, 21.8, 34.6, 34.8, 43.3, 75.4, 112.7, 113.2, 142.9, 143.9; exact mass, m/e 166.1362 (calcd for $C_{11}H_{18}O$, m/e 166.1358). Anal. Calcd for $C_{11}H_{18}O$: C, 79.47; H, 10.91. Found: C, 79.44; H, 10.70.

6-Methylcyclodec-5-enone (1e).[3b] **Method A.** Potassium hydride (24.01% w/w in oil, 131 mg, 0.787 mmol) was washed in a septum-covered flask with dry pentane (2 × 5 mL). Residual solvent was evaporated by a stream of nitrogen, and THF (5 mL) was added to the flask. The alcohol **1d′** (high-R_f material, 109 mg, 0.656 mmol) in THF (4 mL plus a 1-mL rinse) was then injected, and the mixture was stirred at room temperature until evolution of hydrogen ceased (ca. 15 min). The flask was purged with nitrogen while a condenser was connected, and the mixture was refluxed for 15 min. It was then partitioned between pentane (50 mL) and aqueous ammonium chloride (10% w/v, 50 mL), and the aqueous layer was extracted with ether (50 mL). The combined organic phase was washed with saturated aqueous sodium hydrogen carbonate (50 mL) and with brine (50 mL) and was then dried. Evaporation of the solvent and Kugelrohr distillation of the residue [bp 90 °C (0.05 mm)] gave **1e** (104 mg, 95%) better than 97% pure (VPC). Two isomers (ca. 1:8.6)[48] were present, as judged by VPC–mass spectral analysis. They were not separated by TLC (silica impregnated with 5% w/w silver nitrate, 1:4 ethyl acetate–hexane). The mixture had the following: IR (neat) 1704 cm^{-1}; NMR ($CDCl_3$, 200 MHz) δ 1.45–2.21 (m, including a d at 1.73, J = 1.2 Hz, 15 H), 2.27–2.51 (m, 2 H), 4.89–5.05 (m, 0.9 H), 5.08–5.21 (m, 0.1 H); ^{13}C ($CDCl_3$, 50.32 MHz) δ 16.0, 22.5, 25.2, 28.3, 28.4, 40.2, 42.5, 43.5, 129.2, 134.6, 212.5; exact mass, m/e 166.1356 (calcd for $C_{11}H_{18}O$, m/e 166.1357). Anal. Calcd for $C_{11}H_{18}O$: C, 79.47; H, 10.91. Found: C, 79.32; H, 11.09.

The minor isomer, **1e′**, showed a multiplet at δ 5.14 and a broad singlet at δ 1.65 in its 200-MHz NMR spectrum, corresponding to the vinyl and methyl signals, respectively. The corresponding signals for the major isomer were at δ 4.97 and 1.73. Irradiation at δ 1.65 caused enhancement of the multiplet at δ 5.14, while irradiation at δ 1.73 produced no noticeable enhancement of the multiplet at δ 4.97. This NOE experiment establishes the double bond geometry as *E* for the major isomer and *Z* for the minor. The major isomer was identical with an authentic specimen[52] of (5*E*)-6-methylcyclodec-5-enone.

Method B. The above oxy-Cope rearrangement was repeated by using **1d** (low-R_f material, 27.5 mg, 0.166 mmol) in THF (2 mL plus a 1-mL rinse) and potassium hydride (24.01% w/w in oil, 33.2 mg, 0.199 mmol) in THF (5 mL). The workup and Kugelrohr distillation gave **1e** (23.3 mg, 84%) of better than 99% purity (VPC). This material was the *E* isomer:[52] IR (neat) 1701 cm^{-1}; NMR ($CDCl_3$, 200 MHz) δ 1.49–2.27 (m, including a d at 1.73, J = 1.5 Hz, 15 H), 2.29–2.47 (m, 1 H), 4.88–5.09 (m, 1 H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 16.0, 22.5, 25.2, 28.3, 28.4, 40.2, 42.5, 43.5, 129.2, 134.7, 212.5; exact mass, m/e 166.1356 (calcd for $C_{11}H_{18}O$, m/e 166.1357).

(*E*,*E*)-Cyclododeca-2,6-dienone (8d). *trans*-2,3-Diethenylcyclooctanone (**8c**; 150.5 mg, 0.8 mmol) in biphenyl (913 mg) was heated under nitrogen for 20 min in a preheated oil bath at 200 °C. The resulting mixture was applied with the aid of a little hexane to a silica column (2 × 22 cm) made up in hexane. Elution with 1:19 ethyl acetate–hexane gave **8d** (135 mg, 90%) as a homogeneous (TLC, silica impregnated with 15% w/w silver nitrate, 1:4 ethyl acetate–hexane) oil that solidified on cooling: mp 35–36 °C; IR (CCl_4) 1695 cm^{-1}; NMR ($CDCl_3$, 400 MHz) δ 1.10–2.25 (m, 2 H), 1.35–1.52 (m, 2 H), 1.52–1.70 (m, 2 H), 2.00–2.18 (m, 2 H), 2.18–2.34 (m, 4 H), 2.34–2.46 (m, 2 H), 5.0–5.2 [m, incorporating a $^3J \approx 15$ Hz (observed by decoupling experiments), 2 H], 6.11 (d, J = 14 Hz, 1 H), 6.3–6.45 (m, 2 H); ^{13}C NMR ($CDCl_3$, 100.62 MHz) δ 23.1, 24.4, 26.3, 30.3, 31.5, 31.9, 42.5, 130.5, 132.0, 132.3, 144.2, 203.0; exact mass, m/e 178.1356 (calcd for $C_{12}H_{18}O$, m/e 178.1358). Anal. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.81; H, 10.32.

Acknowledgment is made to the Natural Sciences and Engineering Research Council of Canada for support of this work.

Registry No. 1a, 19980-35-9; **1b**, 80533-29-5; **1c**, 63196-62-3; **1c** hydrazone, 80533-30-8; **1d**, 80533-31-9; **1d′**, 80533-32-0; (*E*)-**1e**, 80540-33-6; (*Z*)-**1e′**, 80533-33-1; **2a**, 78828-41-8; **2b**, 78828-44-1; **2c**,

---

(50) Gasanov, A. G.; Mekhtiev, S. D.; Musaev, M. R. *Azerb. Khim. Zh.* **1975**, 6; *Chem. Abstr.* **1976**, *84*, 58704.

(51) This material was enriched in one of the isomers (NMR).

(52) Wharton, P. S. *J. Org. Chem.* **1961**, *26*, 4781. Westen, H. H. *Helv. Chim. Acta* **1964**, 47, 575.

78828-52-1; **3a**, 78828-42-9; **3b**, 80581-36-8; **3c**, 78828-53-2; **4a**, 80533-34-2; **4b**, 78828-47-4; **4c**, 78828-54-3; **5a**, 2816-57-1; **5b**, 78828-48-5; **5c**, 78828-55-4; **6a**, 2408-37-9; **6b**, 80533-35-3; **6c**, 78828-56-5; **7a**, 108-94-1; **7b**, 80533-36-4; **7c**, 1122-25-4; **8a**, 1728-25-2; **8b**, 80533-37-5; **8c**, 80533-38-6; **8d**, 80540-34-7; **9a**, 1502-06-3; **9b**, 80533-39-7; **9c**, 80533-40-0; **10b**, 80533-41-1; **10c**, 58070-37-4; compound;, 80533-42-2; (phenylseleno)acetaldehyde, 71338-48-2; (methylseleno)acetaldehyde, 80533-43-3.

New Method for Coupling Allylic Halides: Use of Te^{2-} Species

Derrick L. J. Clive,* Paul C. Anderson,[†] Neil Moss,[‡] and Alok Singh

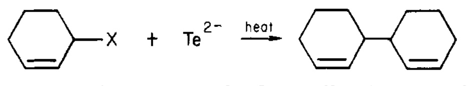
Chemistry Department, University of Alberta, Edmonton, Alberta, Canada, T6G 2G2

Received September 23, 1981

A variety of allylic halides were treated with Te^{2-} (generated in situ) to afford coupled 1,5-dienes (average yield 78% for 11 examples). Mechanistic studies establish that bisallylic tellurides are produced, and these decompose into allylic radicals which then dimerize.

We report a new method for making carbon–carbon bonds that is based on special properties of tellurium not shared, at least in adequate degree, by selenium. The chemistry of selenium has, of course, made an important contribution[1] to synthetic methodology in recent years, but the exploration of tellurium chemistry in this respect is still at an early stage, and there are, as yet, few examples of the controlled manipulation of organic molecules involving the use of tellurium compounds.[2]

We have found that allylic halides[3] react with Te^{2-} to afford coupled products[4] (eq 1, X = Cl or Br). The results in Table I show that the method usually gives synthetically good yields and it is a convenient procedure which illustrates a new aspect of organotellurium chemistry.



(1)

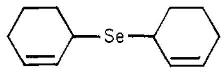
The species Te^{2-} is extremely sensitive to oxygen but it is easy to prepare (see Experimental Section[5]) provided that scrupulous attention is given to the exclusion of air. One simply injects a commercial solution of Super-Hydride[6] onto a stirred portion of powdered tellurium. The metal dissolves in the course of a few hours[7] and addition of the halide,[8] followed by a short period of heating, preferably near 110 °C, completes the sequence. The tellurium precipitates, and the dienes are isolable by chromatography and distillation. In our experience the optimum relative molar proportion is 2.6:1:2 Super-Hydride/tellurium/allylic halide.

The products were identified spectroscopically, although individual assignments of meso and *dl* stereochemistries were not made in most cases.[9] The structures of 14–19 followed from the close correspondence of their ^{13}C NMR spectra to those predicted by empirical methods.[10]

Mechanistic Considerations

Using 3-bromocyclohexene as a test case, we found that the triethylborane present in the reaction mixtures plays no critical role in the process: similar results were obtained by using commercial Na$_2$Te.[11]

The reaction is also one that is characteristic of tellurium. A comparable experiment with 3-bromocyclohexene and Se^{2-} afforded only the selenide **21**, as a mixture of diastereoisomers, and less than 2% (VPC) of 2,2′-bicyclohexenyl was formed even after the reaction period had



21

[†] Natural Sciences and Engineering Research Council of Canada Postgraduate Scholar.

[‡] NSERC Undergraduate Summer Research Award Recipient.

(1) Reviews: (a) Clive, D. L. J. *Tetrahedron* **1978**, *34*, 1049. (b) Reich, H. J. In "Oxidation in Organic Chemistry"; Trahanovsky, W. S., Ed.; Academic Press: New York, 1978; Part C, Chapter 1.

(2) Reviews of tellurium chemistry: (a) Irgolic, K. J. "The Organic Chemistry of Tellurium"; Gordon and Breach Science Publishers Inc.: New York, 1974. (b) Irgolic, K. J. *J. Organomet. Chem.* **1980**, *203*, 367. Synthetic methods based on tellurium chemistry: (c) Clive, D. L. J.; Menchen, S. M. *J. Org. Chem.* **1980**, *45*, 2347 (see also: Still, W. C.; Novack, V. J. *J. Am. Chem. Soc.* **1981**, *103*, 1283). (d) Ley, S. V.; Meerholz, C. A.; Barton, D. H. R. *Tetrahedron, Suppl.* **1981**, *No. 1*, 213. (e) Kambe, N.; Kondo, K.; Ishii, H.; Murai, S.; Sonoda, N. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 547. (f) Uemura, S.; Miyoshi, H.; Okano, M. *Chem. Lett.* **1979**, 1357. (g) Bäckvall, J. E.; Engman, L. *Tetrahedron Lett.* **1981**, 1919. Recent general studies on organotellurium compounds: (h) Clive, D. L. J.; Beaulieu, P. L. *J. Org. Chem.* **1982**, *47*, 1124. (i) Clive, D. L. J.; Chittattu, G. J.; Farina, V.; Kiel, W. A.; Menchen, S. M.; Russell, C. G.; Singh, A.; Wong, C. K.; Curtis, N. J. *J. Am. Chem. Soc.* **1980**, *102*, 4438. (j) Uemura, S.; Fukuzawa, S. *J. Chem. Soc., Chem. Commun.* **1980**, 1033. (k) Kambe, N.; Kondo, K.; Morita, S.; Murai, S.; Sonoda, N. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 1009. (l) Kambe, N.; Kondo, K.; Sonoda, N. *Ibid.* **1980**, *19*, 1009. (m) Bergman, J.; Engman, L. *Synthesis* **1980**, 569. (n) Yamashita, M.; Kato, Y.; Suemitsu, R. *Chem. Lett.* **1980**, 847. (o) Wiriyachitra, P.; Falcone, S. J.; Cava, M. P. *J. Org. Chem.* **1979**, *44*, 3957. (p) Lee, H.; Cava, M. P. *J. Chem. Soc., Chem. Commun.* **1981**, 277. (q) Bergman, J.; Engman, L. *Tetrahedron Lett.* **1978**, 3279. (r) Bonilha, J. B. S.; Petragnani, N.; Toscano, V. G. *Chem. Ber.* **1978**, *111*, 2510. (s) Ramasamy, K.; Kalyanasundaram, S. K.; Shunmugam, P. *Synthesis* **1978**, 545. (t) Barrett, A. G. M.; Read, R. W.; Barton, D. H. R. *J. Chem. Soc., Perkin Trans. 1* **1980**, 2191. (u) Barrett, A. G. M.; Read, R. W.; Barton, D. H. R. *Ibid.* **1980**, 2184. (v) Bergman, J.; Engman, L. *J. Organomet. Chem.* **1980**, *201*, 377.

(3) We have used chlorides and bromides.

(4) For other methods of coupling allylic halides see, for example: (a) Wellmann, J.; Steckhan, E. *Synthesis* **1978**, 901. (b) Reijnders, P. J. M.; Blankert, J. P.; Buck, H. M. *Recl. Trav. Chim. Pays-Bas* **1978**, *97*, 30. (c) Olah, G. A.; Surya Prakash, G. K. *Synthesis* **1976**, 607. (d) Ho, T. L.; Olah, G. A. *Ibid.* **1977**, 170. (e) Kitagawa, Y.; Oshima, K.; Yamamoto, H.; Nozaki, H. *Tetrahedron Lett.* **1975**, 1859. (f) Semmelhack, M. F. *Org. React.* **1972**, *19*, 115. (g) Baker, R. *Chem. Rev.* **1973**, *73*, 487. (h) Benn, R.; Hoffmann, E. G.; Lehmkuhl, H.; Nehl, H. *J. Organomet. Chem.* **1978**, *146*, 103. (i) Okude, Y.; Hiyama, T.; Nozaki, H. *Tetrahedron Lett.* **1977**, 3829. (j) Girard, P.; Namy, J. L.; Kagan, H. B. *J. Am. Chem. Soc.* **1980**, *102*, 2693.

(5) For other preparations of Te^{2-} see ref 2a and: Gysling, H. J. Proceedings of the Third International Symposium on Organic Selenium and Tellurium Compounds, Metz, France, July 1979; Université de Metz: Metz, France, 1981, p 395.

(6) Aldrich trademark for a 1 M solution of lithium triethylborohydride in THF. See: Brown, H. C.; Kim, S. C.; Krishnamurthy, S. *J. Org. Chem.* **1980**, *45*, 1.

0022-3263/82/1947-1641$01.25/0