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Zinc Dust-Cuprous Chloride Promoted Cyclopropanations of Allylic Alcohols Using Ethylidene Iodide

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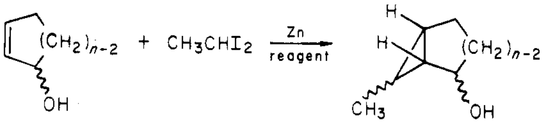
Cyclopropanations of allylic alcohols with ethylidene iodide do not require use of diethylzinc or ethylzinc iodide as previously believed. An ordinary zinc-copper couple, or even more conveniently a zinc dust-cuprous chloride reagent, gives similar yields of methyl-substituted cyclopropylcarbinols after comparable reaction times. However, in reactions of the less reactive olefinic hydrocarbons with ethylidene iodide, diethylzinc and ethylzinc iodide are still the reagents of choice.

As part of our continuing interests[1] in the nature and behavior of bicyclic cyclopropylcarbinyl cation systems, we have needed to carry out Simmons-Smith-type cyclopropanations[2] with ethylidene iodide on a variety of cyclic allylic alcohols to produce methyl-substituted 2-bicyclo[*n*.1.0]alkanols (eq 1). This may be accomplished in satisfactory yields by using the diethylzinc procedure of Kawabata, Furukawa, and co-workers[3] or the related ethylzinc iodide procedure of Sawada and Inouye.[4] However, we have found both procedures to be somewhat inconvenient in that diethylzinc is highly pyrophoric, and the method[5] we have employed for preparing ethereal solutions of ethylzinc iodide gives erratic results.



(1)

Although Simmons, Blanchard, and Smith[6] reported that the reaction of ethylidene iodide with cyclohexene and a zinc-copper couple did not produce 7-methylbicyclo[4.1.0]heptane in a synthetically useful yield, we wondered if this would also be the case with allylic alcohols. Neuman[7] has shown that the reason for the low yield of cyclopropanation product from cyclohexene is due to competing rapid decomposition of the ethylidene iodide derived organozinc reagent to give ethylene (eq 2). However,

$$CH_3CHI_2 \xrightarrow{+Zn(Cu)} CH_3CHI{-}ZnI \xrightarrow{-ZnI_2} CH_2{=}CH_2 \quad (2)$$

allylic alcohols are known[8] to be considerably more reactive in Simmons-Smith cyclopropanations than are simple alkenes such as cyclohexene. Thus, we describe below our investigations into the feasibility of carrying out methylcyclopropanations of allylic alcohols with ethylidene iodide using various zinc couples.

Results and Discussion

To test out the possibility that the reactivities of allylic alcohols might be high enough for cyclopropanation by the ethylidene iodide-zinc couple derived organozinc intermediate to compete successfully with its decomposition, we selected cyclopenten-3-ol (1)[9] for use as a model allylic alcohol. For the zinc reagents we wanted to examine the Le Goff[10] 30-mesh zinc-copper couple, the Rawson and Harrison[11] zinc dust-cuprous chloride procedure, and the Denis, Girard, and Conia[12] 30-mesh zinc-silver couple. All were found in preliminary experiments with cyclopenten-3-ol and methylene iodide, which are described in the Experimental Section, to give good yields of *endo*-2-bicy-

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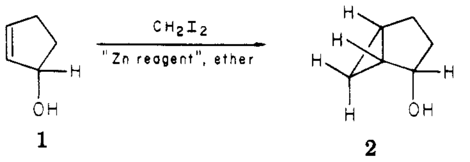
Table I. Reactions of Cyclopenten-3-ol (1) with Ethylidene Iodide and Various Zinc Reagents in Diethyl Ether under Reflux

		6-methyl-*endo*-2-bicyclo[3.1.0]hexanol	
zinc reagent	reaction time,[a] h	% yield[b]	ratio of *anti*- (3) to *syn*-6-methyl (4)[c]
Zn(Cu) (30 mesh)	11[d]	62	78:22
Zn(Ag) (30 mesh)	10[d]	78	76:24
Zn + CuCl (dust)	10[d]	71	76:24
CH_3CH_2ZnI	12[e]	67	73:27

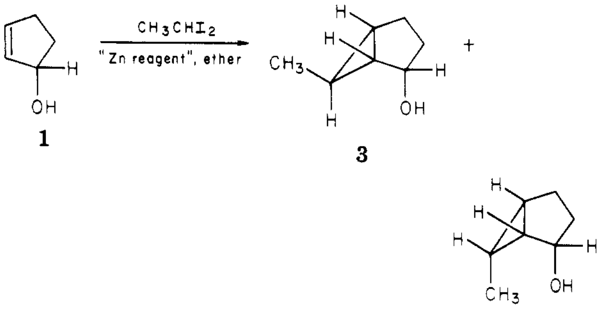
[a] This includes the total time from when mixing of reagents was initially started. [b] Yield of distilled product based on starting cyclopenten-3-ol. [c] Determined by GLC measurements as described in the Experimental Section. [d] Cyclopenten-3-ol (0.05 mol), ethylidene iodide (0.1 mol), and zinc reagent (0.2 mol) in 25 mL of diethyl ether. [e] Cyclopenten-3-ol (0.03 mol), ethylidene iodide (0.06 mol), and ethylzinc iodide (0.2 mol) in 50 mL of diethyl ether.

clo[3.1.0]hexanol (2, eq 3). Thus, none of them possess any inherent problems for use in cyclopropanations of allylic alcohols.



1 2 (3)

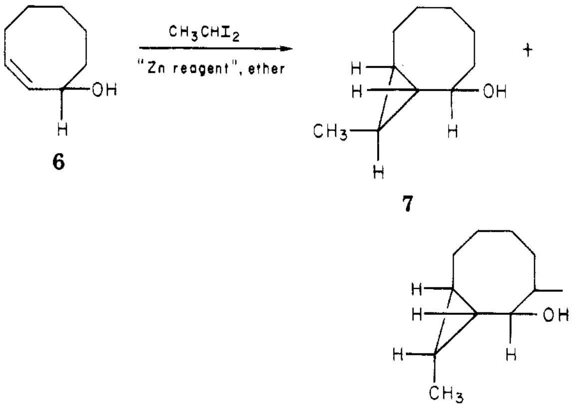
The data in Table I indicate that the 30-mesh zinc-copper and zinc-silver couples as well as the zinc dust-cuprous chloride reagent all afford the 6-methyl-*endo*-2-bicyclo[3.1.0]hexanols **3** and **4** (eq 4) in yields similar to those obtained by using the ethylzinc iodide reagent.[4] The anti to syn ratios for the 6-methyl group were also found to be similar for the different reagents. The stereochemistries of **3** and **4** were established as described in the Experimental Section.



1 **3** **4** (4)

To determine whether the behavior observed with cyclopenten-3-ol is general for all allylic alcohols we carried out reactions with allyl alcohol (**5**) and with cycloocten-3-ol (**6**) using ethylidene iodide and zinc dust-cuprous chloride. These compounds were chosen as representing extremes in allylic alcohol types and because their cyclopropanations with ethylidene iodide had been previously studied[5] by using the diethylzinc reagent. The zinc dust-cuprous chloride reagent was used for these studies because of its operational convenience. It is assumed that the other zinc couples would behave similarly.

In all of the cases the zinc dust-cuprous chloride method gives yields of cyclopropylcarbinol products which are as good as those for the diethylzinc or ethylzinc iodide procedures (Table II). Both methods also give very similar endo-exo and anti-syn product stereochemistries. The 7-methyl-2-bicyclo[6.1.0]nonanol products **7** and **8** (eq 5) were identified by comparisons of their ^1H NMR spectral data with those reported by Kawabata and co-workers[3b] and by lanthanide shift reagent studies. The stereochemistries of the (2-methylcyclopropyl)methanol products obtained from allyl alcohol were proven by comparison of their ^1H NMR spectra and GLC retention times with those of a known sample of *trans*(*anti*)-(2-methylcyclopropyl)-methanol which we synthesized with ^1H NMR data re-



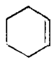
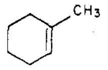
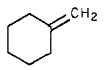
6 **7** **8** (5)

Table II. Yields and Stereochemistries of Products from Cyclopropanations of Several Allylic Alcohols Using Ethylidene Iodide and Zinc Dust-Cuprous Chloride or Diethylzinc-Ethylzinc Iodide Reagents

				rel yields (%) of cyclopropylcarbinols			
				anti-methyl		*syn*-methyl	
allylic alcohol	zinc reagent	reaction time, h	total yield, %	endo	exo	endo	exo
allyl (5)	Zn-CuCl[a]	14	52[b]	74		26	
	$(CH_3CH_2)_2Zn$[c]	10	23[b]	84		16	
cyclopenten-3-yl (1)	Zn-CuCl[a]	10	71[b]	76		24	
	CH_3CH_2ZnI[f]	12	67[b]	73		27	
cycloocten-3-yl (6)	Zn-CuCl[a]	20	88[b]		28		72
	$(CH_3CH_2)_2Zn$[d]	15	76[e]		29		71

[a] Carried out at reflux in the ratio of 0.05 mol of allylic alcohol, 0.11 mol of ethylidene iodide, 0.20 mol of zinc dust, and 0.02 mol of cuprous chloride in 25 mL of diethyl ether. [b] Distilled yield based on starting allylic alcohol. [c] Data of J. Nishimura, N. Kawabata and J. Furukawa (*Tetrahedron*, **1969**, *25*, 2647) for the reaction of 0.20 mol of allyl alcohol, 0.40 mol of ethylidene iodide, and 0.30 mol of diethylzinc in 100 mL of diisopropyl ether at room temperature. [d] Data of N. Kawabata, T. Nakagawa, T. Nakao, and S. Yamashita (*J. Org. Chem.* **1977**, *42*, 3031) for the room-temperature reaction of 10 mmol of *cis*-cycloocten-3-ol, 15 mmol of ethylidene iodide, and 20 mmol of diethylzinc in 10 mL of *cyclohexane* solvent. [e] GLC yield based on starting *cis*-cycloocten-3-ol. [f] Cyclopenten-3-ol (0.03 mol), ethylidene iodide (0.06 mol), and ethylzinc iodide (0.2 mol) in 50 mL of diethyl ether.

Table III. Effect of Olefin Reactivity in Cyclopropanations Using Ethylidene Iodide and Zinc Dust-Cuprous Chloride in Ether[a]

olefin	rel reactivity[b]	reaction time, h	cyclopropanation product	
			% yield	isomeric composn
	1.00	26	5[c]	55:45 mixture[d]
	2.14	20	13[e]	55:45 mixture
	3.84	24	31[e]	one isomer

[a] The reactions were carried out under reflux by using 0.050 mol of alkene, 0.11 mol of ethylidene iodide, 0.15 mol of zinc dust, and 0.015 mol of cuprous chloride in 35 mL of diethyl ether. [b] Data of B. Rickborn and J. H. Chan (*J. Org. Chem.* **1967**, *32*, 3576) for reaction with ICH_2ZnI generated from CH_2I_2 with a zinc-copper couple. [c] GLC yield. [d] A similar mixture of syn-anti products was obtained with diethylzinc by: Nishimura, J.; Kawabata, N.; Furukawa, J. *Tetrahedron* **1969**, *25*, 2647. [e] Distilled yield.

ported by Nishimura and co-workers.[3a]

Finally, having demonstrated that allylic alcohols can be successfully cyclopropanated by using ethylidene iodide and simple, nonethyl-substituted zinc reagents, we briefly examined whether the zinc dust-cuprous chloride reagent could also be used satisfactorily with ethylidene iodide to cyclopropanate olefinic hydrocarbons. The results given in Table III clearly illustrate the direct relationship between olefin reactivity and the yield of cyclopropanation product. However, it must also be concluded that, for cyclopropanations of simple olefinic hydrocarbons with ethylidene iodide, diethylzinc or ethylzinc iodide are still the reagents of choice if high yields are desired.

Experimental Section

General Methods. Melting and boiling points are uncorrected. NMR spectra were run on a Varian Associates A60-A, EM360, or EM 390 instrument with chemical shifts measured in most cases in parts per million (δ) downfield from Me_4Si as an internal standard. GLC analyses and separations were carried out by using Varian Series 1400 and Aerograph A90P3 instruments equipped with Pyrex injector inserts. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, TN. Mass spectra were run at the U.C. Davis Advanced Instrumentation Facility.

Materials. Methylene bromide, methylene iodide, allyl alcohol, crotyl alcohol, cyclohexene, 1-methylcyclohexene, and methylenecyclohexane were obtained commercially and if necessary redistilled before use. Ethylidene iodide,[13] cyclopenten-3-ol,[9] cyclooctén-3-ol,[14] 30-mesh zinc-copper couple,[10] 30-mesh zinc-silver couple,[12] and ethylzinc iodide in ether[5] were prepared as described elsewhere. The zinc dust and the cuprous chloride powder used in the work were Malinckrodt Analytical Reagent quality. Both were used directly from the bottle without any special handling.

Reactions of Cyclopenten-3-ol (1) with Methylene Dihalides. As an example of the usual procedure employed for the preliminary reactions done with the zinc-copper and zinc-silver couples, 0.30 mol of the couple and 30 mL of diethyl ether were placed in a 100 mL round-bottomed, three-necked flask equipped with a magnetic stirrer, a Friedrich condenser, and a dropping funnel. A small portion of 0.22 mol of the methylene dibromide or diiodide was added to the ether-couple mixture, and the remainder was mixed with 0.1 mol of cyclopenten-3-ol and placed into the dropping funnel. The flask was heated until gentle refluxing started, and then slow dropwise addition of the alcohol-methylene dihalide mixture was commenced. The rate of addition and the heating were controlled so as to maintain a normal but not excessive rate of reflux. After the mixture, was heated for various periods of time, an aliquot taken from the reaction mixture was worked up by the slow dropwise addition of saturated aqueous ammonium chloride solution. The ether layer was washed with saturated aqueous sodium carbonate solution, and the ether was then removed by heating. NMR examination of the residual liquid dissolved in carbon tetrachloride was used to determine the extent of conversion of the cyclopenten-3-ol to *endo*-2-bicyclo[3.1.0]hexanol (2). This was done by integrations of the δ 0.5 (m, cyclopropylmethylene), 4.4 (m, carbinol), and 6.0 (t, vinylic) proton regions.[9]

Table IV. Reactions of Cyclopenten-3-ol (1) with a Methylene Dihalide and Various Zinc Reagents in Diethyl Ether under Reflux

zinc reagent	methylene dihalide	reaction time,[a] h	% conversion to 2[b]
Zn(Cu) (30 mesh)[c]	CH_2Br_2	3.5	75
Zn(Cu) (30 mesh)[c]	CH_2I_2	3.2	81
Zn(Ag) (30 mesh)[c]	CH_2I_2	4.5	82
Zn + CuCl (dust)[c]	CH_2I_2	3.2	65
CH_3CH_2ZnI[d]	CH_2I_2	1.5	88

[a] Reaction time includes the time required for dropwise mixing of the reagents. [b] Determined by proton NMR examination of aliquots taken from the reaction mixtures. The results are estimated to be accurate to ±3%. [c] Cyclopenten-3-ol (0.10 mol), methylene dihalide (0.22 mol), and zinc reagent (0.30 mol) in 30 mL of diethyl ether. [d] Cyclopenten-3-ol (0.03 mol), methylene diiodide (0.06 mol), and ethylzinc iodide (0.20 mol) in 50 mL of diethyl ether.

Runs with zinc dust-cuprous chloride were carried out in a similar manner except that the alcohol was added to the zinc dust-cuprous chloride-ether mixture in one portion, and only the methylene iodide was added dropwise. Runs with ethylzinc iodide were done by dropwise addition of the alcohol to the ethylzinc iodide solution in ether followed by dropwise addition of the methylene iodide.

A summary of the results of all of the various reactions is given in Table IV.

Reactions of Cyclopenten-3-ol (1) with Ethylidene Iodide. The reactions of cyclopenten-3-ol with ethylidene iodide reported in Table I were all done by first adding the alcohol to a stirred suspension of the zinc reagent in ether, heating the mixture to reflux, and adding the ethylidene iodide. The final reaction mixtures were worked up by dilution with ether followed by dropwise addition of saturated aqueous NH_4Cl (about 100 mL). The resulting aqueous layer was separated and washed with three 50-mL portions of ether. The combined etheral layers were washed with four 50-mL portions of saturated aqueous Na_2CO_3 and four 25-mL portions of saturated aqueous NaCl, dried over a K_2CO_3-$MgSO_4$ mixture, and distilled. The *anti/syn*-6-methyl-*endo*-2-bicyclo[3.1.0]hexanol product mixture (3 and 4) boiled at 80-83 °C (15 mm).

Anal. Calcd for $C_7H_{12}O$: C, 74.95; H, 10.80. Found: C, 74.81; H, 10.77.

Individual samples of the pure anti-endo and syn-endo isomers were separated by GLC on a 2-m 20% Carbowax 20M on 60/80-mesh nonacid-washed Chromosorb W column. Their *endo*-OH stereochemistries were demonstrated by comparisons of the chemical shift positions and shapes of their 2-proton absorptions with those for the nonmethyl-substituted *endo*- and *exo*-2-bicyclo[3.1.0]hexanols.[9] Their syn-anti stereochemistries were determined with the aid of $Eu(fod)_3$ lanthanide shift reagent by

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observing the effects of the reagent on the chemical shifts of the 6-methyl groups.

For *anti*-6-methyl-*endo*-2-bicyclo[3.1.0]hexanol (3): NMR (CCl_4) δ 0.8–2.0 (m, 7 H), 1.0 (br s, 3 H, CH_3), 3.2 (s, 1 H, OH), 4.5 (m, 1 H, CHOH).

For *syn*-6-methyl-*endo*-2-bicyclo[3.1.0]hexanol (4): NMR (CCl_4) δ 0.7–2.4 (m, 7 H), 1.2 (d, J = 7 Hz, 3 H, CH_3), 3.3 (s, 1 H, OH), 4.8 (m, 1 H, CHOH).

Reaction of Allyl Alcohol with Ethylidene Iodide. The reaction of allyl alcohol with ethylidene iodide and zinc dust–cuprous chloride in ether described in Table II was carried out in a similar manner to that described above for cyclopenten-3-ol. The stereoisomeric (2-methylcyclopropyl)methanol products obtained in a 52% distilled yield were present in a trans/cis (anti/syn) ratio of 74:26; bp 77–79 °C (76 mm) [lit.[3a] bp 134–135 °C (760 mm)].

A sample of the pure *cis*-(2-methylcyclopropyl)methanol was separated from the mixture on a 2-m 20% Carbowax 20M on 60/80-mesh non-acid-washed Chromosorb W column: NMR (CCl_4) δ −0.2 (q, 1 H, cyclopropyl), 0.5–1.2 (m, 3 H, cyclopropyl), 1.0 (d, J = 5 Hz, 3 H, CH_3), 2.3 (s, 1 H, OH), 3.3–3.7 (octet, AB portion of an ABX spin system, 2 H, CH_2OH).

A sample of pure *trans*-(2-methylcyclopropyl)methanol was obtained similarly: NMR (CCl_4) δ 0.01–1.0 (m, 4 H, cyclopropyl), 1.0 (d, J = 5 Hz, 3 H, CH_3), 3.3 (d, J = 7 Hz, 2 H, CH_2OH), 3.6 (s, 1 H, OH).

Reaction of *trans*-Crotyl Alcohol with Dibromomethane. By use of a procedure similar to that described above for cyclopenten-3-ol, the reaction of *trans*-crotyl alcohol with dibromomethane and zinc dust–cuprous chloride for 24 h gave *trans*-(2-methylcyclopropyl)methanol: 68% yield; bp 78–79 °C (78 mm); n^{30}_D 1.4265 [lit.[3a] bp 134–135 °C (760 mm); n^{25}_D 1.4291].

Reaction of Cycloocten-3-ol (6) with Ethylidene Iodide. The reaction of cycloocten-3-ol (6) with ethylidene iodide and zinc dust–cuprous chloride in ether described in Table II was carried out in a similar manner to that described above for cyclopenten-3-ol; bp 105–106 °C (10 mm). The two isomeric alcohol products were separated on a 2-m 10% diethylene glycol succinate on 60/80-mesh non-acid-washed Chromosorb W column. For *anti*-9-methyl-*exo*-2-bicyclo[6.1.0]nonanol (7): NMR (CCl_4) δ 0.2–2.2 (m, 13 H), 1.1 (d, J = 6 Hz, 3 H, CH_3), 2.3 (s, 1 H, OH), 3.2 (m, 1 H, CHOH). For *syn*-9-methyl-*exo*-2-bicyclo[6.1.0]nonanol (8): NMR (CCl_4) δ 0.5–2.1 (m, 13 H), 1.1 (br s, 3 H, CH_3), 1.2 (s, 1 H, OH), 3.5 (m, 1 H, CHOH).

Reactions of Cyclohexene, 1-Methylcyclohexene, and Methylenecyclohexane with Ethylidene Iodide. The reactions of these materials with zinc dust–cuprous chloride in ether reported in Table III were all carried out by following procedures similar to those employed for the reaction of cyclopenten-3-ol reported above. The crude reaction mixtures obtained after workup were examined by GLC on a 97-m SE-30 glass capillary column and then distilled.

For the cyclohexene reaction, the scale and yield were so small that no materials could be obtained by distillation. However, GLC examination revealed that approximately a 5% yield of a mixture of *syn*- and *anti*-7-methylbicyclo[4.1.0]heptanes[3a] had been obtained.

For the 1-methylcyclohexene reaction, a 13% distilled yield of a mixture of isomeric 1,7-dimethylbicyclo[4.1.0]heptanes was obtained; bp 60–75 °C (70 mm). No attempt was made to determine the product stereochemistries. A precise mass spectrometric molecular weight was determined: calcd for C_9H_{16} m/e 124.1253, found m/e 124.1255.

For the methylenecyclohexane reaction, a 31% distilled yield of cyclopropyl product was obtained as one isomer: bp 70–78 °C (77 mm); NMR (CCl_4) δ −0.2 (t, 1 H, cyclopropyl), 0.2–0.7 (m, 2 H, cyclopropyl), 0.7–2.2 (m, 10 H), 1.0 (d, J = 6 Hz, 3 H, CH_3). A precise molecular weight was determined by mass spectrometry: calcd for C_9H_{16} m/e 124.1253, found m/e 124.1246.

Acknowledgment. We acknowledge support for this work in part by a Faculty Research Grant to E.C.F. from the Committee on Research of the University of California, Davis, and in part by an Earl C. Anthony Grant to G.B.

Registry No. 1, 3212-60-0; 2, 822-58-2; 3, 80865-50-5; 4, 80865-51-6; 5, 107-18-6; 6, 3212-75-7; 7, 62929-18-4; 8, 62861-98-7; ethylidene iodide, 594-02-5; *cis*-(2-methylcycloproply)methanol, 21003-35-0; *trans*-(2-methylcyclopropyl)methanol, 21003-36-1; *trans*-crotyl alcohol, 504-61-0; dibromomethane, 74-95-3; cyclohexene, 110-83-8; 1-methylcyclohexene, 591-49-1; methylenecyclohexane, 1192-37-6; *syn*-7-methylbicyclo[4.1.0]heptane, 14135-43-4; *anti*-7-methylbicyclo[4.1.0]heptane, 14222-39-0; 1,7-dimethylbicyclo[4.1.0]heptane, 80924-08-9; 1-methylspiro[2.5]octane, 41417-81-6; methylene iodide, 75-11-6; zinc, 7440-66-6; cuprous chloride, 7758-89-6.

Selenium-Stabilized Carbanions.[1] Synthesis of Enals and Silyl Enones Using 1,3-Bis(phenylseleno)propene

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The utility of 1,3-bis(phenylseleno)propene (4) as a propenone synthon having n_3 (1) or n_1 and n_3 (3) reactivity has been examined. Deprotonation of 4 with lithium diisopropylamide in THF at −78 °C proceeds to give a lithium reagent which reacts smoothly with alkyl halides (isopentyl bromide, 2-bromobutane), epoxides (propylene oxide, cyclohexene oxide), carbonyl compounds (isobutyraldehyde, 4-*tert*-butylcyclohexanone, 3-pentanone), and trimethylsilyl chloride. The products are smoothly converted to 3-substituted propenal derivatives in 71–88% yield by oxidation with 4 equiv of hydrogen peroxide in dichloromethane. The reaction product with acetone has also been converted to 1-(phenylseleno)-4-methyl-1,3-pentadiene by reductive elimination of the groups PhSeOH. Deprotonation of 3-(trimethylsilyl)-1,3-bis(phenylseleno)propene with lithium diethylamide gives a reagent which can be alkylated (2-bromopropane, 2-bromobutane, 2-methyl-1-bromopropane) and hydroxyalkylated (acetone) with good regioselectivity. Oxidation of these products (7) with peracetic acid gives 3-substituted 1-(trimethylsilyl)propenones (8, vinyl silyl ketones). The anions prepared from 4 and 6 show exceptional nucleophilicity compared to other synthetically equivalent reagents, and the unmasking of the propenone moiety can be accomplished under unusually mild conditions.

A number of reagents for umpolung of the normal reactivity of the propenone moiety such that C-3 has nucleophilic character (n_3 reactivity,[3] 1) have been developed.[4] These include the lithium reagent from metalation of