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Selenium Stabilized Carbanions. α-Lithio Selenoxides as Reagents for the Synthesis of Olefins, Allyl Alcohols, and Dienes[1]

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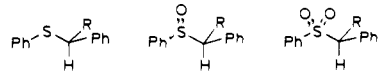
Abstract: Techniques for the preparation of α-lithio selenoxides have been developed. These reagents react cleanly with most aldehydes and ketones to give β-hydroxy selenoxides, which can be thermolyzed to allyl alcohols or reduced to β-hydroxy selenides. The β-hydroxy selenides are further transformed to olefins by reductive elimination. α-Lithio selenoxides can also be alkylated and acylated, although these reactions are of lesser scope and usefulness than the reaction with aldehydes and ketones. A synthesis of 1,1-bis(phenylseleno)cyclopropane was developed based on an intramolecular alkylation of an α-lithio selenoxide. The compound is a suitable precursor for the preparation of 1-phenylselenocyclopropyllithium, which was used to prepare cyclopropyl phenyl selenide and 1-phenylselenocyclopropanecarboxylic acid.

Heteroatom stabilized organometallic reagents are powerful tools for the formation of functionalized carbon–carbon bonds. The most widely used reagents of this type are the phosphonium ylides (Wittig reagents), although sulfonium ylides and phosphorus, sulfur, and to a lesser extent silicon stabilized anions have become increasingly important. Developments in the preparation and reactions of selenium stabilized lithium and other organometallic reagents have been fostered by the interesting and useful chemistry available to selenides and selenoxides.[3] In the preceding paper[4] the chemistry of α-lithio selenides was presented. We report here the results of our study of the preparation and reactions of α-lithio selenoxides.

The incentive for the study of α-lithio *selenoxides* is provided by the lack of satisfactory procedures for the general preparation of α-lithio *selenides* by deprotonation of selenides, a result of the limited acidifying power of the phenylseleno group, and the propensity of selenides to be fragmented upon treatment with powerful metalating agents. The substantially greater acidity expected for selenoxides, however, should allow their deprotonation in cases where the corresponding selenides are insufficiently acidic. The greater acidity of selenoxide vs. selenide can be inferred from comparisons with kinetic and thermodynamic acidity data available for sulfides, sulfoxides, and sulfones. Bordwell and co-workers[5] have reported the following pK_a data (Me_2SO solvent and references).

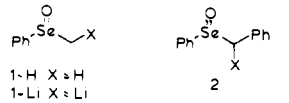


R = Ph	26.7	24.5	22.3
R = H	30.8		23.4

Since most alkyl selenoxides are at best only marginally stable at room temperature,[6] it is not surprising that deprotonations and pK_a studies of selenoxides had not been attempted. In addition to their thermal instability, selenoxides have physical properties which present difficulties in manipulation. They are extremely polar. Many are hygroscopic and tenaciously retain water of hydration.[7] As a result, the lower alkyl selenoxides are sufficiently water soluble that significant losses can accompany an aqueous workup.

Results and Discussion

Preparation of α-Lithio Selenoxides. To assess the viability of these reagents as synthetic intermediates, exploratory work was carried out with the relatively stable selenoxides, **1**-H and **2**-H, and the derived lithium reagents, **1**-Li and **2**-Li. Methyl



1-H X = H
1-Li X = Li

2

phenyl selenoxide (**1**-H) could be prepared by ozonization of methyl phenyl selenide in dichloromethane. Purification of the selenoxide beyond simple removal of solvent led to decomposition or the essentially irreversible absorption of water of hydration. For this reason, an in situ generation of the lithio compound is preferable for **1**-Li; the procedure is described below.

In contrast benzyl phenyl selenoxide (**2**-H) is more tractable: it can easily be obtained anhydrous and crystalline.[8] Deprotonation of **2**-H with lithium diisopropylamide (LDA) in THF at −78 °C appears to lead smoothly to the α-lithio selenoxide **2**-Li as indicated by the formation of olefins upon alkylation and selenoxide syn elimination (see Table II). The more easily prepared α-lithio selenide[4,9] analogous to **2**-Li would seem to be preferable for most applications since it is a better nucleophile. The only exception might be in a situation where an easily oxidized function was present in the electrophile.

Our approach to the preparation of lithium reagents from thermally labile selenoxides involves the low-temperature oxidation of selenides and in situ deprotonation of the resultant selenoxides. The oxidant for this purpose must be reactive at low temperatures under anhydrous conditions, must not leave byproducts which interfere with subsequent organometallic reactions, and must be compatible with ether solvents. Of many reagents available for the conversion of selenides to selenoxides (O_3, RCO_3H, H_2O_2, $NaIO_4$, $PhICl_2/H_2O$, Cl_2, Br_2/H_2O, N_2O_4, $Tl(NO_3)_3$, *t*-BuOOH),[3a] only two, ozone and *m*-chloroperbenzoic acid, met these requirements.

Ozone has a long history as a convenient oxidant for the preparation of selenoxides.[10] Further oxidation to selenone can

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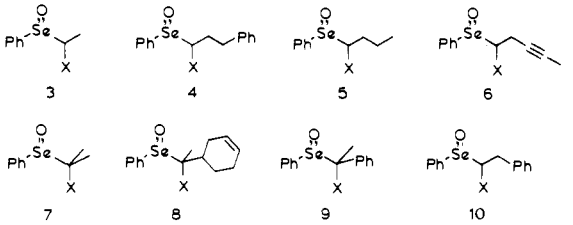
occur,[11] but requires temperatures of 0 °C or higher and long reaction times. The ozonization of selenide at −78 °C stops cleanly at the selenoxide stage. In the absence of easily oxidized solvents or functional groups a blue end point signaling excess ozone marks the completion of the oxidation. Unfortunately tetrahydrofuran (THF), which is often the preferred solvent for formation and reaction of organolithium reagents, reacts sufficiently rapidly with ozone that no such end point is seen. A titrated ozone stream must therefore be used in THF. Diethyl ether is sufficiently unreactive toward ozone so that a blue end point is seen and hence is the most convenient solvent when this oxidant is to be used.

m-Chloroperbenzoic acid (MCPBA) oxidizes all of the phenyl alkyl selenides we have encountered in both THF and dichloromethane in less than 10 min at −10 °C or 30 min at −78 °C. The MCPBA can be added as a solid at −10 °C, but addition in solution is preferable at −78 °C to ensure complete oxidation since the peracid is only slightly soluble at this temperature.

The deprotonation of selenoxides in THF occurs within a few minutes at −78 °C upon the addition of LDA. Two equivalents of base is used since 1 equiv is consumed to form lithium *m*-chlorobenzoate, which does not appear to interfere with subsequent reactions. The onset of carbanion formation as LDA is added is indicated by a yellow color, the appearance of which can be used as an indicator for complete deprotonation of the *m*-chlorobenzoic acid and any other protic materials present.

This procedure has been used to form α-lithio selenoxides (**3–10**, X = Li) from a variety of primary and secondary selenoxides.



The reactions of α-lithio selenoxides with electrophiles are summarized in Scheme I. The intermediate selenoxides (**11–13**) are normally not isolated but are directly converted to olefins by selenoxide syn elimination or to selenides by reduction.

Synthesis of Allyl Alcohols. The addition of α-lithio selenoxides to most aldehydes and ketones is complete in 10 min at −78 °C. Partial enolization of the carbonyl compound has been observed during the reaction of **3**-Li and **7**-Li with 2-methylcyclohexanone, but this is normally not a significant problem.

α,β-Unsaturated carbonyl compounds undergo predominantly 1,2 addition (run 11, Table I, and runs 6, 7, Table III)

Scheme I

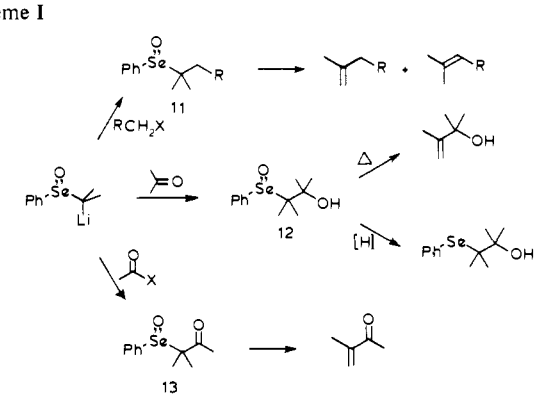
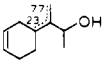
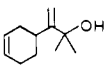
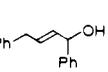
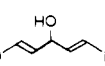
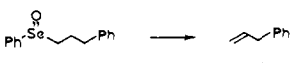


Table I. Preparation of Allyl Alcohols by Reaction of α-Lithio Selenoxides with Ketones and Aldehydes Followed by Syn Elimination

RUN NO	LITHIUM REAGENT	ALDEHYDE KETONE	ALLYL ALCOHOL	YIELD[a]
1	3			66
2	7			85[b]
3	7			55[b]
4	5			78
5	6			68[c]
6	8			81
7	8			74
8	9			74
9	4			81[b] 76
10	4			72[b]
11	10			74

[a] Yields are overall based on selenide. Unless specified otherwise *m*-chloroperbenzoic acid was used as oxidant. [b] Selenide was oxidized by low-temperature ozonization. [c] A mixture of *E* and *Z* isomers was obtained.

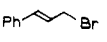
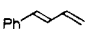
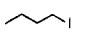
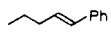
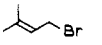
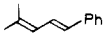
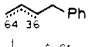
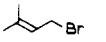
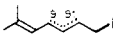
although some systems (such as 1-phenylpropen-1-one) do give substantial amounts of Michael addition. Attempts to induce exclusive 1,4 addition in the presence of copper salts were not successful. The β-hydroxy selenoxides thus formed lead to allyl alcohols upon pyrolysis (Table I). It soon became clear that syn eliminations of alkyl selenoxides were subject to several kinds of side reactions. The yields of allylbenzene **14** on thermolysis of the selenoxide **4**-H serve to illustrate the problem.



Elimination Conditions	% of Yield of 14
CH_2Cl_2, -78° to 25°, 1.5 hrs	13
CH_2Cl_2, Py(2 eq), -78° to 25°, 1.5 hr	23
CCl_4, reflux, 5 min	74
CCl_4, iPr_2NH (2 eq), reflux, 5 min	>95

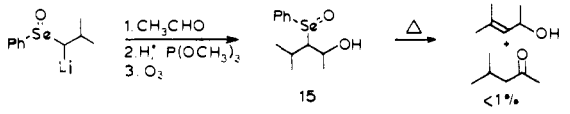
The major side reactions we observed were reduction of **4**-H to the selenide and reactions of the benzeneselenenic acid formed with **14**. Optimum yields were obtained when a cold solution of the selenoxide was added to refluxing carbon tetrachloride or hexane containing at least 1 equiv of an alkylamine. These conditions have been successfully applied for the conversion of a variety of selenoxides to olefins[12] and are even required in some situations for the preparation of enones.[13] The intricacies of selenoxide syn elimination chemistry have been dealt with in a recent paper.[6c]

Table II. Alkylation of α-Lithio Selenoxides

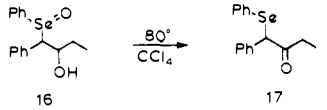
RUN NO.	LITHIUM REAGENT	ALKYL HALIDE	OLEFIN	YIELD[a]
1	1[b]			75
2	2[c]			81
3	2[c]			88
4	4[b]	CH_3I		59
5	4[b]			81

[a] Olefin yields are overall from selenoxide. [b] Lithium reagent prepared by in situ oxidation and deprotonation. [c] Lithium reagent prepared by deprotonation of benzyl phenyl selenoxide.

The regioselectivity of selenoxide syn eliminations has an important bearing on the synthetic methodology reported here. There is a pronounced preference for β-hydroxy selenoxides to give allyl alcohols instead of enols. This selectivity, which is also observed to some extent for amine oxide pyrolyses,[14] was first reported by Sharpless and Lauer[15] in connection with the conversion of olefins or epoxides to allyl alcohols via β-hydroxy selenides. We have carefully examined compound **15** (prepared as shown, mixture of diastereomers) and have detected no



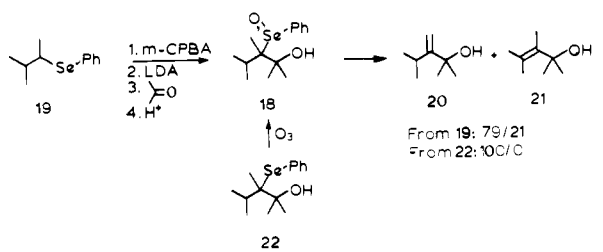
ketone (<1%) upon thermolysis. The reaction was done in the presence of diethylamine to trap benzeneselenenic acid which can otherwise react with the enol as formed.[6c] For example, selenoxide **16** gives the phenylseleno enone **17** when pyrolyzed.[4]



Takahashi, Nagashima, and Tsuji[16] have made a similar observation.

Selenoxides normally show a preference for elimination toward the least substituted carbon and for the formation of conjugated over unconjugated olefins. Several examples in Tables I (runs 6, 7) and II (runs 4, 5) illustrate these trends. A more interesting case is outlined in Scheme II. Here the selenoxide **18** (prepared by addition of the α-lithio selenoxide derived from **19** with acetone) gave a 79/21 ratio of the olefins **20** and **21**. When **18** was prepared by ozonization of the selenide **22** and pyrolysis, only **20** was formed. The difference in behavior may be attributed to different diastereomer ratios in the starting selenoxide **18**. The equilibration of configurations at the selenoxide, normally a rather facile process,[7,8] is hampered by the unusual steric crowding in **18**. Similarly, diastereomeric steroidal selenoxides have been reported to undergo different rates of syn eliminations,[6b] and one diastereomer of an allylic selenoxide apparently undergoes syn elimination

Scheme II



whereas the other undergoes a [2,3] sigmatropic rearrangement.[17] Pronounced stereochemical effects on the regiochemistry of sulfoxide syn eliminations have also been reported.[18]

We have detected only trans isomers for disubstituted double bonds (Table I, runs 4, 9, 10), except for run 5, where a 62/38 ratio is formed. This is a consequence of the small size of the acetylene substituent. α,β-Unsaturated nitriles prepared by selenoxide syn elimination also give mixtures of stereoisomers.[19]

The synthesis of allyl alcohols as described above is synthetically equivalent to the addition of a vinyl anion to a ketone or aldehyde. The principal advantage over a classical vinyllithium or vinyl Grignard reaction is in the availability of the starting material: alkyl selenides are easily prepared from alkyl halides or alcohols, in contrast to the difficulty of obtaining all but the simplest *vinyl* halides. While the compounds in runs 1 and 3 of Table I are easily prepared using vinyllithium or 2-propenyllithium, others such as the compounds prepared in runs 6 and 7 would not be so easily assembled using vinyl organometallic reagents. Furthermore, it is likely that the α-lithio selenoxide preparation is compatible with a wider variety of functionalities.

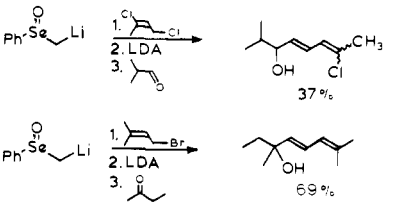
Vinylboranes have been used as vinyl anion equivalents either by a direct reaction with aldehydes (but not ketones), or by a reaction of the vinylborane with $LiCH_2SCH_3$ followed by oxidation of the allylborane product.[20] These methods, while providing for good stereochemical control at the double bond, are more limited in scope than the present procedure.

The synthesis of allyl alcohols by addition of α-lithio *selenides* to carbonyl compounds has been reported by Seebach[21] and Krief.[22] Although it is likely that these lithium reagents have better nucleophilic properties (i.e., less enolization of ketones) than the α-lithio selenoxides, they are in general not as easily prepared.

The synthesis of allyl alcohols by an analogous procedure employing α-lithio sulfoxides has recently been reported.[25] The thermolysis of β-hydroxy sulfoxides was carried out in refluxing xylene in the presence of base.

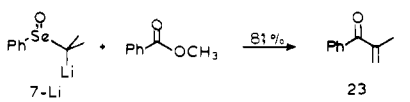
Alkylation of α-Lithio Selenoxides. The reaction of α-lithio selenoxides with allyl bromides and methyl iodide occurs at −78 °C. Unfortunately the utility of this process is constrained by the lack of regioselectivity of the subsequent syn elimination. As shown in Table II, two olefins are formed unless structural features provide only a single elimination pathway.

Dienols can be prepared by a one-pot reaction in which the anion of methyl phenyl selenoxide is first alkylated, deprotonated, and then treated with a carbonyl compound. The overall



transformation corresponds to the addition of a dienyl anion to the carbonyl compound. Although the procedure is experimentally exacting, it does provide very rapid access to compounds of this type.

Enones by Acylation of α-Lithio Selenoxides. It is possible to acylate α-lithio selenoxides, but yields are unsatisfactory except in special circumstances. For example, compound **23** is isolated in good yield, but attempts to acylate **7**-Li with acyl



halides, anhydrides, or aliphatic esters gave much lower yields of enones as did reaction of methyl benzoate with lithium reagents derived from primary selenoxides. Successful acylation of α-lithio selenides has been reported by Denis, Dumont, and Krief.[23]

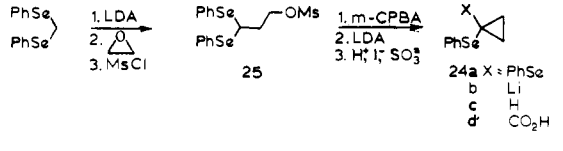
Olefins by Reductive Elimination of β-Hydroxy Selenides. In the preceding paper[4] the conversion of β-hydroxy selenides to olefins by reductive elimination of PhSeOH using methanesulfonyl chloride/triethylamine was described. The synthesis of hydroxy selenides using α-lithio selenoxides requires a method for the reduction of the intermediate β-hydroxy selenoxides under mild conditions such that syn elimination does not occur. We have developed two such procedures.

Selenoxides are easily reduced. For the present application the reaction mixture containing the β-hydroxy selenoxide was first acidified with acetic acid or propionic acid (the latter is preferable because of greater solubility at low temperature). This serves two functions: the rate of selenoxide syn eliminations is decreased in the presence of strong hydrogen bond donors,[6c] and the reduction is more rapid in the presence of acid. The acidified reaction mixture is then treated with either sodium iodide and bisulfite or trimethyl phosphite. The latter reagent is more reactive and should be used with particularly unstable selenoxides. We have also found that $POCl_3/SnCl_2$ can be used as both a reducing agent for the selenoxides and for reductive elimination of the β-hydroxy selenide. The two-step procedure using $RCO_2H/P(OMe)_3$ followed by $MeSO_2Cl/NEt_3$ is experimentally more convenient.

The examples in Table III illustrate some olefins we have prepared via α-lithio selenoxides. Compounds such as the tetrasubstituted olefins in runs 4 and 5 are not easily available by procedures involving Wittig reagents (enolization occurs). Not directly illustrated in Table III is another attractive feature of these reactions: the excellent nucleophilic properties of PhSe allow for the preparation of the requisite starting selenides even in sterically hindered situations (e.g., compound **19**) for which one might anticipate a great deal of difficulty in preparing analogous phosphonium salts or phosphonates. Benzeneselenolate ($PhSe^-$) is 5000 times as nucleophilic as $P(Ph)_3$ and 350 000 times as nucleophilic as $P(OCH_3)_3$ toward methyl iodide.[24] One might expect these ratios to be even larger for a sterically hindered alkyl halide.

The selenoxide syn elimination or PhSeOH reductive elimination[4] gives diphenyl diselenide as the major selenium-containing product. It is often convenient to remove this and other selenium-containing materials by oxidation of the products with hydrogen peroxide in dichloromethane. It should be emphasized that $H_2O_2/PhSeO_2H$ is capable of causing epoxidation of tri- and tetrasubstituted olefins,[26] as well as Baeyer–Villiger oxidation of ketones.[27] Oxidative cleanup of reaction mixtures should be carried out with this fact in mind.

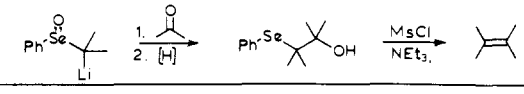
1-Phenylselenocyclopropyllithium. To examine the synthetic potential of 1-phenylselenocyclopropyllithium (**24b**)[28] we undertook the synthesis of two possible precursors: 1,1-bis(phenylseleno)cyclopropane (**24a**) and cyclopropyl phenyl selenide (**24c**).[29] The most successful route is shown below; the key step involves cyclization of the monoselenoxide prepared from mesylate **25.** Compound **24a** was isolated in 57% overall yield starting with bis(phenylseleno)methane.

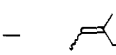
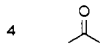
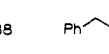
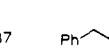
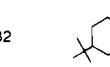
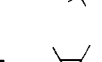
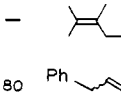
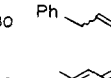


Treatment of **24a** with *n*-BuLi gave solutions of lithium reagent **24b**, which could be protonated to give **24c** and carboxylated to give 1-phenylseleno-1-carboxycyclopropane (**24d**).

Cyclopropyl phenyl selenide could not be deprotonated with LDA, lithium 2,2,6,6-tetramethylpiperidide, or lithium diethylamide in tetrahydrofuran.

Table III. Olefins Prepared from α-Lithio Selenoxides by Reductive Elimination of β-Hydroxy Selenides



RUN NO.	α-LITHIO SELENOX.	KETONE ALDEHYDE	YIELD[a]	OLEFIN	YIELD
1	3		—		71[b]
2	4		88		73
3	4		87		74
4	7		82		94
5	7		—		71[b]
6	10		80		80
7	10		56		52

[a] Yield of β-hydroxy selenide (%). [b] Overall yield.

Summary

α-Lithio selenoxides are versatile synthetic intermediates for the preparation of a variety of olefins including allyl alcohols and dienes. Depending on subsequent transformations, they function as either vinyl anion equivalents or as reagents for a Wittig-like olefin synthesis, applicable even to the preparation of tetrasubstituted ethylenes.

Experimental Section

General. Nuclear magnetic resonance (NMR) spectra were obtained on JEOL MH-100, FX-60, or Bruker WH-270 spectrometers. Infrared (IR) spectra were obtained on a Perkin-Elmer IR-267 spectrophotometer and mass spectra (MS) on an AEI MS-902 spectrometer. Unless specified otherwise NMR spectra were measured in CCl_4 solution and IR spectra of neat liquid between salt plates were recorded. Elemental analyses were performed by Spang Microanalytical Laboratories and Galbraith Laboratories. Melting and boiling points are uncorrected.

Normal workup procedure involved addition of the reaction mixture to 30 mL of 5% Na_2CO_3 solution and extraction with 2 × 30 mL of 50% ether/pentane. The combined organic portions were washed with 1.2 N HCl solution and saturated $NaHCO_3$ solutions, if amine is present, and with saturated NaCl solution and dried by filtering through a cone of Na_2SO_4. Solvent was removed on a rotary evaporator at reduced pressure.

Preparative thin layer chromatography (TLC) was carried out using Merck PF-254 silica gel. Dry column chromatography was carried out using MCB 60 silica gel. All reactions involving organolithium reagents, selenols, or selenolate anions were run under an atmosphere of dry nitrogen. Apparatus for anhydrous reactions was dried in a 110 °C oven for at least 3 h.

Diisopropylamine and diethylamine were distilled from potassium hydroxide and stored over 4A molecular sieves. Tetrahydrofuran (THF) was freshly distilled from lithium aluminum hydride or sodium benzophenone ketyl. Solutions of lithium diisopropylamide (LDA), 1 M in THF/hexane, were prepared as in ref 13. *m*-Chloroperbenzoic acid (MCPBA) obtained from various commercial sources was found to contain *m*-chlorobenzoic acid and water as major impurities, which

may be removed by recrystallization from hexane (3 g/65 mL).

Caution. Organoselenium compounds are toxic and should be handled with care.

Preparation of Selenides. Alkyl phenyl selenides were synthesized according to literature methods[4,30] from the appropriate halide or mesylate using $PhSe^-$ in ethanol, prepared by reduction of the diselenide with either $NaBH_4$ or Rongalite (sodium formaldehyde sulfoxylate). Several model procedures are presented below.

Isopropyl Phenyl Selenide. Powdered $NaBH_4$ (1.6 g, 42 mmol) was added in portions to a solution of 6.24 g (20 mmol) of Ph_2Se_2 in 100 mL of EtOH under N_2 until the solution was colorless. Isopropyl chloride (5 mL) in 5 mL of EtOH was added, the solution was refluxed for 20 h, poured into 10% HCl, and extracted with pentane, and the combined extracts were washed, dried (Na_2SO_4), and distilled to give 7.25 g (91% yield, bp 44–46 °C (0.3 mm), lit.[31] bp 97 °C (16 mm)) of isopropyl phenyl selenide: NMR δ 1.38 (d, J = 7 Hz, 6 H), 3.36 (septet, J = 7 Hz,1H), 7.1–7.6 (m, 5 H).

Phenyl 3-Phenylpropyl Selenide. Phenyl 3-phenylpropyl selenide (4.6 g, 84% yield) was prepared by the same procedure as given for isopropyl phenyl selenide using 3.12 g (10 mmol) of Ph_2Se_2, $NaBH_4$ (0.9 g, 24 mmol), and 1-bromo-3-phenylpropane (4.2 g, 20.6 mmol). The selenide was purified by distillation (Kugelrohr, 112°C, 0.06 mm): NMR δ 1.91 (quintet, J = 7 Hz, 2 H), 2.62 (t, J = 7 Hz, 2 H), 2.75 (t, J = 7 Hz, 2 H), 7.0–7.4 (m, 10 H); IR 3058, 3020, 2930, 1578, 1492, 1475, 1450, 1436, 1072, 1021, 737, 695 cm^{-1}.

Anal. Calcd for $C_{15}H_{16}Se$: C, 65.45; H, 5.86. Found: C, 65.43; H, 5.83.

1-(3-Cyclohexenyl)ethyl Phenyl Selenide. To an ether solution of CH_3MgI prepared from 4.05 g (0.167 mol) of Mg and 24.2 g (0.167 mol) of CH_3I was added dropwise 14.66 g (0.133 mol) of 3-cyclohexene-1-carboxaldehyde at such a rate as to maintain gentle refluxing of the reaction mixture. The solution was stirred for 0.5 h and 10 mL of saturated NH_4Cl solution was slowly added. The reaction mixture was poured into saturated NH_4Cl solution, extracted with ether/pentane, washed with saturated NaCl solution, dried, and concentrated. **1-(3-Cyclohexenyl)ethanol** was isolated (14.3 g, 85% yield) by distillation (bp 97–100 °C, 12 mm): NMR δ 1.15 (d, J = 7 Hz, 3 H), 1.2–2.2 (m, 7 H), 3.52 (m, 2 H), 5.64 (broad s, 2 H).

Methanesulfonyl chloride (11.4 g, 0.1 mol) was added to a cooled (0 °C) solution of 11.45 g (0.091 mol) of 1-(3-cyclohexenyl)ethanol in 350 mL of CH_2Cl_2 containing 13.77 g (0.14 mol) of NEt_3 over a period of 10 min. After stirring for 15 min the reaction mixture was washed with ice/water, cold 10% HCl, saturated $NaHCO_3$, and saturated NaCl solution. The solid **1-(3-cyclohexenyl)ethyl mesylate** (18.1 g, 98% yield) obtained after drying and evaporation of solvent was used for the next reaction without further purification.

Diphenyl diselenide (12.5 g, 0.04 mol), sodium formaldehyde sulfoxylate (6.2 g, 0.4 mol), and 130 mL of EtOH were heated to 50 °C under N_2 atmosphere. NaOH solution (5 M, 26 mL) was added and the mixture was stirred for 0.5 h. When the yellow color of Ph_2Se_2 had disappeared 18.1 g (0.089 mol) of the mesylate obtained above, dissolved in 30 mL of EtOH, was added. After stirring overnight at 50°C, the reaction mixture was poured into 10% HCl and extracted with pentane. The combined extracts were washed with saturated $NaHCO_3$ and saturated NaCl solution and dried. The filtrate was distilled after removal of solvent to give 16.04 g (76% yield) of **1-(3-cyclohexenyl)-ethyl phenyl selenide** (bp 105–110 °C, 0.04 mm): NMR δ 1.39 and 1.42 (d, J = 7 Hz, 3 H), 1.85 (m, 3 H), 2.07 (m, 4 H), 3.25 (m, 1 H), 5.63 (broad s, 2 H), 7.2–7.6 (m, 5 H); IR 3030, 2925, 1580, 1479, 1428, 1025, 740, 693 cm^{-1}; MS M^+ 266.057 37 (calcd, 266.057 37).

1-Phenylseleno-3-butyne. Methanesulfonyl chloride (1.1 mL, 14 mmol) was added dropwise to a CH_2Cl_2 (25 mL) solution containing 0.766 g (10 mmol) of 3-butyn-1-ol and 2.1 mL (15 mmol) of NEt_3 at 0 °C. This solution was stirred for 20 min, worked up using CH_2Cl_2, and distilled (Kugelrohr) to give 1.437 g (97% yield) of **3-butyn-1-yl mesylate** (bp 60–63 °C, 0.05 mm): NMR δ 1.97 (t, J = 2.5 Hz, 1 H), 2.62 (td, J = 7, 2.5 Hz, 2 H), 3.0 (s, 3 H), 4.24 (t, J = 7 Hz, 2 H).

In a 50-mL two-neck flask, 1.414 g (4.5 mmol) of Ph_2Se_2, 0.7 g (4.5 mmol) of sodium formaldehyde sulfoxylate (Rongalite), and 20 mL of EtOH were heated to 50 °C under N_2. To this solution was added 3 mL of 5 M NaOH solution and it was stirred at 50 °C for 20 min; during this time the yellow color disappeared. An EtOH (1 mL) solution of 1.332 g (9 mmol) of 3-butyn-1-yl mesylate was added to this solution, which was stirred at this temperature for 30 min. The reaction mixture was poured into 10% HCl solution, worked up, and distilled (Kugelrohr, bp 60–62 °C, 0.05 mm) giving 1.1 g (58% yield) of 1-phenylseleno-3-butyne: NMR δ 1.87 (t, J = 2.6 Hz, 1 H), 2.48 (td, J = 7.5 and 2.6 Hz, 2 H), 2.94 (t, J = 7.5 Hz, 2 H), 7.2–7.7 (m, 5 H); IR 3300, 3060, 2940, 2110, 1580, 1480, 1440, 735, 690 cm^{-1}.

1-Phenylseleno-3-pentyne. LDA (1 M, 4.2 mL) was added to a THF (10 mL) solution of 0.836 g (4 mmol) of 1-phenylseleno-3-butyne at −78 °C. After 5 min CH_3I (0.4 mL, 6.4 mmol) and 0.8 mL of HMPA were added to this solution, and the cold bath was removed. After 1 h the reaction mixture was worked up. The concentrated solution was distilled (Kugelrohr, bp 70–71 °C, 0.05 mm) to give 0.675 g (76% yield) of 1-phenylseleno-3-pentyne: NMR δ 1.72 (t, J = 2.5 Hz, 3 H), 2.48 (m, 2 H). 2.98 (t, J = 8 Hz, 2 H), 7.2–7.7 (m, 5 H).

Anal. Calcd for $C_{11}H_{12}Se$: C, 59.20; H, 5.42. Found: C, 59.40; H, 5.53.

Benzyl Phenyl Selenoxide (2-H). Ozone was bubbled into a CH_2Cl_2 (20 mL) solution of 2.46 g (10 mmol) of benzyl phenyl selenide at −78 °C until the solution was pale blue. Excess ozone was removed by bubbling in dry N_2 and 10 mL of CCl_4 was added. Benzyl phenyl selenoxide[8] (2.55 g, 96% yield) crystallized from this solution upon concentration and cooling: NMR δ 3.91 and 4.16 (AB, J_{AB} = 12 Hz, 2 H), 6.96 (m, 2 H), 7.23 (m, 3 H), 7.42 (s, 5 H).

1-Vinylcyclohexanol (Table I, Run 1). *m*-Chloroperbenzoic acid (4.04 g, 85% pure, 20 mmol) was added to a cooled (−15 °C) solution of 2.8 mL (20 mmol) of ethyl phenyl selenide in 50 mL of THF under an atmosphere of dry nitrogen. After 20 min the reaction mixture was cooled to −78 °C and 44 mL of 1 M LDA solution was slowly added. (After addition of 23 mL of LDA solution, the yellow color of the anion persisted.) After 5 min 2.0 mL (19.5 mmol) of cyclohexanone was added. The yellow color faded in 10 min and the solution was stirred for 0.5 h. Water (1.5 mL) and HOAc (2 mL) dissolved in 5 mL of THF were added to the reaction mixture. The cold reaction mixture was slowly added to a vigorously stirred solution of 150 mL of hexane and 3 mL of diispropylamine maintained at reflux. The solution was refluxed for 5 min after the addition was complete and poured into 200 mL of 5% Na_2CO_3 solution and the layers were separated. The aqueous layer was washed with 2 × 200 mL of ether/pentane. The combined organic extracts were washed with 1.2 N HCl solution and saturated NaCl solution, dried, and concentrated on a rotary evaporator (bath temperature <20 °C).

The concentrate was dissolved in 50 mL of CH_2Cl_2 in a flask equipped with a reflux condenser. Water (4 mL) and pyridine (2 mL) were added. A solution of H_2O_2 (30%, 1 mL) was added to the vigorously stirred mixture. Within 5 min solvent had started to reflux on the sides of the flask indicating that the reaction had started. The flask was cooled in an ice/water bath and three portions of 1 mL each of 30% H_2O_2 were added over the next 20 min. The reaction mixture was stirred for 15 min, poured into 150 mL of saturated $NaHCO_3$ solution, and extracted with 2 × 200 mL of 50% ether/pentane. The combined organic extracts were washed with 1.2 N HCl solution and saturated NaCl solution and dried. The concentrated filtrate upon distillation gave 1.66 g (68% yield) of 1-vinylcyclohexanol[32] (bp 57–58 °C, 5 mm): NMR δ 1.15–1.85 (m, 10 H), 4.94 (dd, J = 10, 2 Hz, 1 H), 5.16 (dd, J = 17, 2 Hz, 1 H) 5.9 (dd, J = 17, 10 Hz); IR 3400, 2940, 2860, 1645, 1450 cm^{-1}; MS M^+ 126.104 76 (calcd, 126.104 46).

2-Methyl-1-phenyl-2-propen-1-ol (Table I, Run 2). Ozone was bubbled into an ether (15 mL) solution of 0.83 mL (5 mmol) of isopropyl phenyl selenide at −78 °C until the solution was pale blue. Anhydrous N_2 gas was passed through the solution to remove excess ozone, and 5 mL of THF and 5.5 mL of 1 M LDA solution were added to the selenoxide at −78 °C. After 20 min, when all the selenoxide had dissolved, giving a clear yellow solution, benzaldehyde (0.56 mL, 5.5 mmol) was added. After 15 min 2 mL of 10% acetic acid in THF was added and the cold solution was dropped into 40 mL of refluxing CCl_4 containing 0.7 mL of i-Pr_2NH. The yellow solution was worked up. The filtrate was concentrated and 0.05 mL of NEt_3 was added. Preparative TLC using 20/79/1 ether/pentane/NEt_3 gave 0.63 g (85% yield) of 2-methyl-1-phenyl-2-propen-1-ol:[33] NMR broad singlets at δ 1.56 (3 H), 1.9 (1 H), 4.86 (1 H), 5.0 (1 H), 5.1 (1 H); IR 3460, 3060, 2970, 1490, 1450, 1215, 695 cm^{-1}; MS M^+ 148.088 02 (calcd, 148.088 81).

1-(1-Butenyl)cyclohexanol (Table I, Run 4). Using the same procedure as for run 1, 0.875 mL (5 mmol) of *n*-butyl phenyl selenide in 10 mL of THF was oxidized with MCPBA (1.01 g, 85%, 5 mmol) and deprotonated with 11 mL of 1 M LDA solution, and the anion formed was treated with 0.515 mL (5 mmol) of cyclohexanone. The selenoxide

was thermolyzed, and Ph_2Se_2 was oxidized with H_2O_2. Kugelrohr distillation of the product gave 0.601 g (78% yield) of 1-(1-butenyl)-cyclohexanol (bath temperature 38–40 °C (0.03 mm)): NMR δ 1.0 (t, J = 7 Hz, 3 H), 1.16 (broad s, 1 H), 1.46 (m, 10 H), 2.06 (qd, J = 7, 5 Hz, 2 H), 5.51 (d, J = 15 Hz), 5.71 (dt, J = 15, 5 Hz, 1 H); IR 3400, 2940, 1665, 1450, 1210 cm^{-1}.

Anal. Calcd for $C_{10}H_{18}O$: C, 77.87; H, 11.76. Found: C, 77.76; H, 11.68.

2-Methyloct-4-en-6-yn-3-ol (Table I, Run 5). *m*-Chloroperbenzoic acid (0.202 g, 1 mmol) was added to a cooled (−78 °C) solution of 0.215 g (0.96 mmol) of 1-phenylseleno-3-pentyne in 3 mL of THF. This solution was stirred for 0.5 h, and 2.3 mL of 1 M LDA was added. Isobutyraldehyde (1 mmol) was added to this yellow-orange solution. After 20 min a solution of 0.2 mL of HOAc in 2 mL of THF was added and the cold reaction mixture was added dropwise to 15 mL of CCl_4 containing 0.1 mL of *i*-Pr_2NH under reflux. The crude product obtained after normal workup (with 1 drop of NEt_3) was purified by preparative TLC using 20/79/1 ether/pentane/NEt_3 as solvent to give 88 mg (68% yield) of a 62/38 mixture of (*E*)- and (*Z*)-2-methyloct-4-en-6-yn-3-ol; NMR ($CDCl_3$, 270 MHz) *E* isomer δ 0.90 (d, J = 7.0 Hz, CH_3), 0.925 (d, J = 6.8 Hz, CH_3), 1.7 (m, CH), 1.9 (broad s, OH), 1.94 (d, J = 2.4 Hz, CH_3), 3.88 (t, J = 6.3 Hz, CH), 5.65 (dqd, J = 16.0, 2.3, 1.3 Hz, CH), 6.05 (dd, J = 16.0, 6.6 Hz, CH); *Z* isomer δ 0.91 (d, J = 6.8 Hz, CH_3), 0.98 (d, J = 6.9 Hz, CH_3), 1.8 (m, CH), 1.9 (broad s, OH), 1.97 (d, J = 2.4 Hz, CH_3), 4.36 (dd, J = 6.5, 8.3 Hz, CH), 5.57 (dqd, J = 11, 2.3, 1.3 Hz, CH), 5.82 (dd, J = 10.9, 8.5 Hz, CH); IR 3400, 2960, 2205, 1470 cm^{-1}; MS M^+ 138.1045 (calcd, 138.1045).

3-(3′-Cyclohexenyl)-3-buten-2-ol (Table I, Run 6). *m*-Chloroperbenzoic acid (85% pure, 0.404 g, 2 mmol) was added to a THF solution of 0.428 mL (2 mmol) of 1-(3′-cyclohexenyl)ethyl phenyl selenide maintained at −20 °C. After 20 min, the reaction mixture was cooled to −78 °C and 4.4 mL of 1 M LDA was added. After 5 min, 0.15 mL (2.7 mmol) of freshly distilled acetaldehyde was added to this yellow solution and stirred for 15 min. A solution of 0.4 mL of HOAc and 0.4 mL of H_2O in 4 mL of THF was added and the resulting suspension was added to a magnetically stirred solution of 0.3 mL (2.15 mmol) of *i*-Pr_2NH in 20 mL of hexane maintained at reflux. The crude product obtained after normal workup was purified by preparative TLC using 20/79/1 ether/pentane/NEt_3 to give 0.266 g (81% yield) of a mixture containing 77% of 3-(3′-cyclohexenyl)-3-buten-2-ol and 23% of 3-(3′-cyclohexylidene)-3-buten-2-ol as determined by NMR: 3-(3′-cyclohexenyl)-3-buten-2-ol δ 1.19 (d, J = 7 Hz, 3 H), 1.7 (m, 2 H), 2.0–2.5 (m, 6 H), 4.31 (q, J = 7 Hz, 1 H), 4.85 (s, 1 H), 5.12 (s, 1 H), 5.69 (broad s, 2 H); 3-(3-cyclohexylidene)-3-buten-2-ol δ 1.10 (d, J = 7 Hz, 3 H), 1.64 (broad s, 3 H), 2.0–2.5 (m, 5 H), 2.71 (broad s, 2 H), 4.8 (q, J = 7 Hz, 1 H); IR 3400, 2940, 1655 cm^{-1}; MS M^+ 152.1198 (calcd, 152.1201).

2-Methyl-3-(3′-cyclohexenyl)-3-buten-2-ol (Table I, Run 7): NMR δ 1.31 (s, 6 H), 1.4–2.4 (m, 8 H), 4.74 (s, 1 H), 5.11 (s, 1 H), 5.62 (broad s, 2 H); IR 3450, 3040, 2950, 1640, 1445 cm^{-1}.

2-Methyl-3-phenyl-3-buten-2-ol[34] (Table I, Run 8): NMR δ 1.34 (s, 6 H), 4.90 (broad s, 1 H), 5.40 (broad s, 1 H), 7.3 (m, 5 H).

2-Methyl-5-phenyl-3-penten-2-ol (Table I, Run 9): NMR δ 1.04 (s, 6 H), 2.14 (broad s, 1 H), 3.28 (d, J = 5 Hz, 2 H), 5.34 (d, J = 16 Hz, 1 H), 5.72 (dt, J = 16 and 5 Hz, 1 H), 7.12 (m, 5 H); IR 3400, 3020, 2970, 1600, 1492, 1450, 695 cm^{-1}; MS M^+ 176.120 28 (calcd, 176.120 11).

(*E*)-1,4-Diphenyl-2-butenol. (*E*)-1,4-Diphenyl-2-butenol (0.161 g) was prepared from 0.212 mL (1 mmol) of phenyl 3-phenylpropyl selenide and 0.105 mL (1.03 mmol) of benzaldehyde following the procedure given for 2-methyl-1-phenyl-2-propenol (run 2) in 72% yield. It was purified by preparative TLC using 20/79/1 ether/pentane/NEt_3: NMR δ 1.64 (broad s, 1 H), 3.32 (d, J = 6 Hz, 2 H), 5.04 (d, J = 6 Hz, 1 H), 5.67 (m, 2 H), 7.0–7.3 (m, 10 H); IR 3380, 3020, 2970, 1595, 1490, 1450, 695 cm^{-1}; MS M^+ 224.119 75 (calcd, 224.120 11).

1,5-Diphenyl-1,4-penten-3-ol (Table I, Run 11). A solution of 2-phenylethyl phenyl selenide (0.261 g, 0.188 mL, 1.0 mmol) in THF at −78 °C was treated with MCPBA (85% pure, 0.204 g, 1.0 mmol), Deprotonation with 2.1 mL of 1 M LDA and addition to cinnamaldehyde (0.132 g, 0.126 mL, 1.0 mmol) afforded the β-hydroxy selenoxide which was thermolyzed according to the procedure in run 2. The crude product was purified by preparative TLC, eluting twice with 10/89/1 ether/pentane/NEt_3 to give 0.176 g (74% yield) of 1,5-diphenyl-1,4-penten-3-ol:[35] R_f 0.1; NMR δ 2.99 (broad s, 1 H), 4.85 (t, J = 6 Hz, 1 H), 6.18 (dd, J = 6, 16 Hz, 2 H), 6.55 (d, J = 16 Hz, 2 H), 7.19 (m, 10 H).

Thermolysis of 4-Methyl-3-phenylselenino-2-pentanol (15). *m*-Chloroperbenzoic acid (85% pure, 0.4 g, 2 mmol) was added to a cooled (−15 °C) solution of 0.34 mL (2 mmol) of isobutyl phenyl selenide in 5 mL of THF. After 15 min the solution was cooled to −78 °C and 4.4 mL of 1 M LDA was added. Freshly distilled acetaldehyde (0.15 mL, 2.5 mmol) was added to the yellow solution and it was stirred for 20 min. The selenoxide **15** was reduced by addition of 1/4 HOAc/THF and 0.24 mL (2 mmol) of trimethyl phosphite to the reaction mixture. The cold bath was removed after 15 min and the solution was allowed to warm up to room temperature and worked up. The concentrated filtrate with 0.03 mL of NEt_3 upon preparative TLC using 20/79/1 ether/pentane/NEt_3 furnished 0.483 g (94% yield) of 4-methyl-3-phenylseleno-2-pentanol: NMR δ 0.96 (J = 6 Hz) and 1.24 (d, J = 6 Hz, 3 H), 2.08 (m, 1 H), 2.52 (broad s, 1 H), 2.96 (m, 1 H), 3.88 (q, J = 6 Hz, 1 H), 7.1–7.7 (m, 5 H); ^{13}C NMR in $CDCl_3$ δ 19.1, 20.8, 21.4, 22.0, 22.5, 30.2, 31.0, 67.2, 68.5, 68.7, 69.0, 127.0, 129.0, 131.1, 133.7, 133.8; IR 3440, 2950, 1525, 1475, 750, 730, 685 cm^{-1}; MS M^+ 258.0525 (calcd, 258.0523).

A solution of 30 mg of 4-methyl-3-phenylseleno-2-pentanol in 0.5 mL of alcohol-free $CDCl_3$ was ozonized at −55 °C and $MeNH_2$ was bubbled into the sample at −55 °C for 15 s. The NMR tube containing this sample of **15** was heated at 60 °C for 1.75 h and the products were checked by NMR (no peak at 2.04 ppm) and IR.

An analogous experiment was done on a sample of 4-methyl-3-phenylseleno-2-pentanol (30 mg) which contained 0.7 mg of 4-methyl-2-pentanone [NMR δ 0.91 (d, J = 7 Hz, 6 H), 2.04 (s, 3 H), 2.22 (m, 3 H)] and the products were checked. A comparison of these two results indicated that >99% of the elimination occurred away from the hydroxyl group and 4-methyl-2-pentanone did not decompose under the reaction conditions.

Thermolysis of 2,3,4-Trimethyl-3-phenylselenino-2-pentanol (18, Scheme II). Reaction between 3-methyl-2-phenylselenobutane (**19**, 0.19 mL, 1 mmol) and acetone (0.60 mL, 1 mmol) according to the procedure given above (oxidation with MCPBA, reduction with $(MeO)_3P$) gave a mixture of alcohols. Preparative TLC of this mixture furnished 64 mg (22.4%) of 2,3,4-trimethyl-3-phenylseleno-2-pentanol (**22**) [NMR δ 1.03 (s, 3 H), 1.14 (d, J = 6.5 Hz, 3 H), 1.25 (d, J = 6.5 Hz, 3 H), 1.34 (s, 6 H), 2.1 (m, 1 H), 2.93 (broad s, 1 H), 7.1–7.8 (m, 5 H); IR 3460, 2960, 1580, 1480, 735, 685 cm^{-1}] and 38 mg (29.7%) of a mixture (79:21) of **20**[34] [NMR δ 1.08 (d, J = 7 Hz, 6 H), 1.35 (s, 6 H), 2.49 (m, 1 H), 4.87 (s, 1 H), 5.12 (s, 1 H)] and **21** [NMR δ 1.45 (s, 6 H), 1.68 (broad s, 6 H), 1.95 (broad s, 3 H)].

1-Phenyl-1-pentene (Table II, Run 2). To a stirred suspension of 1.048 g (4 mmol) of benzyl phenyl selenoxide in 12 mL of THF was added 5.9 mL of 0.7 M LDA solution at −78 °C. After 5 min 0.47 mL (4.1 mmol) of butyl iodide was added to the red solution and stirred for 1 h. The reaction mixture was warmed to room temperature and stirred for 1.5 h. Distillation of the product after normal workup gave 0.47 g (81% yield) of 1-phenyl-1-pentene[36] (bath temperature 30–31 °C, 0.15 mm): NMR δ 0.95 (t, J = 7 Hz, 3 H), 1.46 (sextet, J = 7 Hz, 2 H), 2.12 (q, J = 7 Hz, 2 H), 6.04 (dt, J = 16, 7 Hz, 1 H), 6.28 (d, J = 16 Hz, 1 H), 7.0–7.4 (m, 5 H); IR 3020, 2960, 1596, 1490, 1450, 735, 690 cm^{-1}.

4-Methyl-1-phenyl-1,3-pentadiene (Table II, Run 3). 4-Methyl-1-phenyl-1,3-pentadiene[37] was prepared by following the procedure given for (*E*)-1-phenyl-1-pentene (run 2) from 0.263 g (1 mmol) of benzyl phenyl selenoxide and 0.200 g (1.25 mmol) of 1-bromo-3-methyl-2-butene in 88% yield purified by short-path distillation (bath temperature 60–65 °C, 0.2 mm); NMR δ 1.83 (broad s, 6 H), 5.9 (d, J = 11 Hz, 1 H), 6.29 (d, J = 15 Hz, 1 H), 6.83 (dd, J = 15, 11 Hz, 1 H), 7.0–8.4 (m, 5 H); IR 3030, 2910, 1642, 1595, 1450, 692 cm^{-1}.

4-Phenyl-1-butene (Table II, Run 4). Phenyl 3-phenylpropyl selenide (0.212 mL, 1 mmol) was ozonized and deprotonated by following the procedure for Table I, run 2. Methyl iodide (0.070 mL, 1.1 mmol) was added to the solution of anion **4**-Li, and the mixture was stirred for 15 min, quenched with 0.5 mL of 1/10 HOAc/THF, and added to refluxing CCl_4 containing 0.14 mL (1 mmol) of *i*-Pr_2NH. After normal workup the concentrated filtrate was dissolved in 3 mL of CH_2Cl_2 and treated with 0.25 mL of 30% H_2O_2, 0.25 mL of water, and 0.1 mL of pyridine to remove Ph_2Se_2. Preparative TLC of crude product afforded 77 mg (59% yield) of olefin which was a 64:36 mixture of 4-phenyl-1-butene[38] and 4-phenyl-2-butene as determined by NMR: 4-phenyl-1-butene δ 2.37 (q, J = 7 Hz, 2 H), 2.69 (t, J =

7 Hz, 2 H), 4.98 (m, 2 H), 5.49 (m, 1 H), 7.1 (m, 5 H); 4-phenyl-2-butene δ 1.67 (broad d, J = 5 Hz, 3 H), 3.18 (broad d, J = 6 Hz, 2 H), 5.7 (m, 2 H), 7.1 (m, 5 H).

2-Methyl-7-phenyl-2,5-heptadiene (Table II, Run 5). To a cooled (−15 °C) solution of 2.18 mL (10 mmol) of phenyl 3-phenylpropyl selenide in 25 mL of THF was added 2.02 g (85% pure, 10 mmol) of MCPBA. After the solution was stirred for 15 min under a N_2 atmosphere, the flask was cooled to −78 °C and 22 mL of 1 M LDA solution was added. After 5 min 1.3 mL (10 mmol) of 1-bromo-3-methyl-2-butene was added to the yellow solution and stirred for 0.5 h. A white precipitate had developed after 20 min. After another 10 min 2 mL of a 25% aqueous acetic acid solution was added and the reaction mixture was dropped into a refluxing solution of 1.5 mL of i-Pr_2NH in 100 mL of hexane with efficient stirring. The solution was refluxed for 5 min after the addition was complete, and the product mixture was worked up.

The crude product was dissolved in 30 mL of CH_2Cl_2 in a flask equipped with a reflux condenser. Pyridine (1 mL), water (2 mL), and 1 mL of H_2O_2 solution (30%) were added. The flask was cooled to 0 °C when dichloromethane started to reflux on the sides of the flask (ca. 5 min). Two portions of 0.5 mL each of 30% H_2O_2 solution were added in 10 min. The reaction mixture was stirred until the yellow color of Ph_2Se_2 had disappeared (ca. 10 min) and worked up. Kugelrohr distillation (bp 60–65 °C, 0.06 mm) gave 1.48 g (80% yield) of a diene mixture containing 9% of 2-methyl-7-phenyl-2,5-heptadiene [identified by NMR resonances at δ 1.69 (broad s) and 3.28 (m)] and 91% of 2-methyl-7-phenyl-2,4-heptadiene: NMR δ 1.72 (broad s, 6 H), 2.38 (q, J = 7 Hz, 2 H), 2.69 (t, J = 7 Hz, 2 H), 5.56 (m, 2 H), 6.17 (dd, J = 15, 10 Hz, 1 H); ^{13}C NMR in $CDCl_3$ δ 18.16, 25.84, 34.72, 36.16, 125.1, 125.7, 127.25, 128.19, 128.3, 130.62, 132.77, 141.83; IR 3020, 2920, 1600, 1492, 1450, 695 cm^{-1}; MS M^+ 186.1405 (calcd, 186.1409).

3,7-Dimethyl-4,6-octadien-3-ol. m-Chloroperbenzoic acid (85% pure, 0.406 g, 2 mmol) was added in portions to a THF solution of 0.242 mL (2 mmol) of methyl phenyl selenide at −10 °C. After 15 min the solution was cooled to −78 °C and 4.5 mL of 1 M LDA was added. After 5 min, 0.21 mL (2.04 mmol) of 1-bromo-3-methyl-2-butene was added to the reaction mixture and stirred for 0.5 h. LDA (1 M, 2 mL) was added to the reaction mixture followed by 0.2 mL (2.2 mmol) of 2-butanone. After stirring for 20 min, 1 mL of 1/5 HOAc/THF was added. The cold solution was dropped into 40 mL of refluxing CCl_4 containing 0.3 mL of i-Pr_2NH. Workup followed by preparative TLC gave 0.212 g (69% yield) of 3,7-dimethyl-4,6-octadien-3-ol;[39] NMR δ 0.87 (t, J = 7 Hz, 3 H), 1.25 (s, 3 H), 1.56 (q, J = 7 Hz, 2 H), 1.8 (s, 6 H), 3.02 (broad s, 1 H), 5.62 (d, J = 15 Hz, 1 H), 5.85 (d, J = 10 Hz, 1 H), 6.45 (dd, J = 10 and 15 Hz, 1 H); IR 3420, 2980, 2940, 1660 cm^{-1}; MS M^+ 154.1356 (calcd, 154.1358).

7-Chloro-2-methyl-4,6-octadien-3-ol: NMR δ 0.87 (d, J = 7 Hz, 3 H), 0.91 (d, J = 7 Hz, 3 H), 1.71 (octet, J = 7 Hz, 1 H), 2.16 (s, 3 H), 3.12 (broad s, 1 H), 3.85 (t, J = 6.5 Hz, 1 H), 5.48 (dd, J = 15 and 6.5 Hz, 1 H), 6.05 (d, J = 10 Hz) and 6.14 (d, J = 10 Hz, 1 H), 6.46 (dd, J = 15 and 10 Hz, 1 H); IR 3440, 2970, 1655 cm^{-1}; MS M^+ 174.0813 (calcd, 174.0811).

2-Methyl-1-phenyl-2-propen-1-one (23). Ozone was passed through a well-stirred solution of 1.63 mL (10 mmol) of isopropyl phenyl selenide in 30 mL of ether at −78 °C until the ether was pale blue. Excess ozone was removed by bubbling in N_2, and 10 mL of THF was added. LDA (1 M, 11 mL) was added and the solution was stirred for 20 min to give a yellow solution of **7**-Li. Methyl benzoate (1.1 mL, 8.8 mmol) was added at once to the reaction mixture and stirred for 0.5 h at −78 °C. The reaction mixture was quenched with 2 mL of 1/10 HOAc/THF and then added to 50 mL of refluxing CCl_4 containing 1.5 mL of i-Pr_2NH. The crude product obtained after normal workup was distilled to give a 1.17-g fraction (bp 42–44 °C, 0.2 mm) which was 90% pure 2-methyl-1-phenyl-2-propen-1-one:[40] NMR δ 2.02 (m, 3 H), 5.52 (m, 1 H), 5.78 (m, 1 H), 7.17–7.8 (m, 5 H); IR 1661, 1628, 1600, 1580 cm^{-1}; MS M^+ 146.0728 (calcd, 146.0732).

Preparation of β-Hydroxy Selenides. A General Method (Table III). To a stirred solution of alkyl aryl selenide (1 mmol.) in 2 mL of THF at −78 °C under N_2 was added MCPBA (85% pure, 0.204 g, 1 mmol) in 1 mL of THF. After 15 min 2.1 mL of 1 M LDA was added to the selenoxide solution; the reaction mixture turned deep yellow from formation of lithio selenoxide. After 5 min the carbonyl compound was added neat. (A solution of carbonyl compound in THF was generally used for a compound which was a solid or for a large-scale reaction (i.e., greater than 5 mmol).) The reaction mixture was stirred at −78 °C for 5–7 min (shorter time for aldehydes). The β-hydroxy selenoxide thus generated was reduced and purified by one of the following methods.

1. To the mixture was slowly added 3.5 mL of 1/10 HOAc/THF (6 mmol). The reaction mixture was warmed to 0 °C and removed from N_2 atmosphere. Sodium iodide (0.30 g, 2 mmol) in 1 mL of water cooled to 0 °C was added. (Vigorous stirring was necessary owing to the presence of lithium alkoxides.) The reaction mixture turned dark brown. After 15 min saturated $NaHSO_3$ in water was added dropwise until the reaction mixture became a pale yellow. It was stirred for an additional 15 min and poured into 5 mL of saturated $NaHSO_3$ and 15 mL of 50% ether/pentane. The organic phase was washed with 10% Na_2CO_3 and aqueous NaCl, dried over Na_2SO_4, and concentrated at reduced pressure.

2. To the mixture was added slowly 1.5 mL of 50% propionic acid/THF followed by the dropwise addition of trimethyl phosphite (0.263 g, 0.25 mL, 2.12 mmol). The reaction mixture was warmed to room temperature over a 1-h period whereupon it was poured into 5 mL of water and 15 mL of 50% ether/pentane. The organic phase was washed with 10% NaOH until it was alkaline. It was further washed with saturated $NaHCO_3$ and NaCl solutions, dried over Na_2SO_4, and concentrated at reduced pressure.

The crude product was generally purified by preparative TLC using 10% ether/pentane. Those systems which were acid sensitive, i.e., tertiary alcohols, were treated with a few drops of NEt_3 before application to the plate, and the eluting solvent was made 1% in NEt_3.

3-Methyl-5-phenyl-2-pentene (Table III, Run 1). 3-Methyl-2-phenylseleno-5-phenyl-3-pentanol was prepared from ethyl phenyl selenide (3.70 g, 0.020 mol) and 4-phenyl-2-butanone (2.96 g, 0.020 mol) according to the general procedure using a trimethyl phosphite reduction. The crude β-hydroxy selenide was used in the next step without further purification: NMR (mixture of diastereomers) δ 1.23, 1.28 (s, 3 H), 1.50 (d, J = 7 Hz, 3 H), 1.70–1.97 (m, 2 H), 2.43 (s, 1 H), 2.52–2.94 (m, 2 H), 3.23–3.57 (m, J = 7 Hz, 1 H), 6.97–7.41 (m, 8 H), 7.41–7.71 (m, 2 H); MS M^+ 334.0829 (calcd, 334.0836).

The crude selenide was converted to olefin following the literature procedure[4] using NEt_3 (10.1 g, 14.0 mL, 0.100 mol) and $MeSO_2Cl$ (6.90 g, 4.65 mL, 0.060 mol). The crude product mixture was dissolved in 40 mL of ether and 10 mL of 30% hydrogen peroxide and 60 mL of $NaHCO_3$ added (epoxidation of the olefin can occur here[26]). After stirring for 1 h, followed by a basic workup, the product mixture showed olefin contaminated with Ph_2Se_2. Elution of the crude product through a column of silica gel separated the olefin from 4-phenyl-2-butanone. Purification by Kugelrohr distillation (bath 34 °C, 0.13 mm) afforded 2.29 g (71% yield) of the olefin as a clear oil; NMR (mixture of E/Z isomers) δ 1.30–1.82 (m, 6 H), 2.34 (m, 2 H), 2.72 (m, 2 H), 5.24 (broad q, 1 H), 7.16 (m, 5 H).

Anal. Calcd for $C_{12}H_{16}$: C, 90.51; H, 9.49. Found: C, 90.55; H, 9.55.

2-Methyl-6-phenyl-2-pentene (Table III, Run 2). The β-hydroxy selenide was prepared from 3-phenylpropyl phenyl selenide (0.273 g, 0.218 mL, 1.0 mmol) and acetone (0.071 g, 0.090 mL, 1.2 mmol) according to the general procedure. An $NaI/NaHSO_3$ reduction of the selenoxide was used. The crude product, upon purification by preparative TLC using 10/89/1 ether/pentane/NEt_3, gave 0.292 g (88% yield) of the β-hydroxy selenide as an oil: R_f 0.15; NMR δ 1.17 (s, 3 H), 1.20 (s, 3 H), 1.51–2.35 (m, 2 H), 2.41 (s, 1 H), 2.50–2.80 (m, 1 H), 2.82–3.18 (m, 2 H), 6.87–7.33 (m, 8 H), 7.33–7.67 (m, 2 H).

The crude 2-methyl-3-phenylseleno-5-phenyl-2-pentanol (0.292 g, 0.877 mmol) in CH_2Cl_2 was treated with NEt_3 (0.443 g, 0.63 mL, 4.38 mmol) and $MeSO_2Cl$ (0.303 g, 0.204 mL, 2.63 mmol) according to the general procedure. An NMR yield of 73% olefin[41] was determined by a comparison with an internal standard: NMR δ 1.53 (s, 3 H), 1.66 (s, 3 H), 2.28 (broad q, J = 7 Hz, 2 H), 2.60 (broad t, J = 7 Hz, 2 H), 5.14 (broad t, J = 7 Hz, 1 H), 7.26 (s, 5 H).

1-Isopropylidene-4-*tert*-butylcyclohexane (Table III, Run 4). The β-hydroxy selenide was prepared from isopropyl phenyl selenide (0.279 g, 0.205 mL, 1.4 mmol) and 4-*tert*-butylcyclohexanone (0.154 g, 1.0 mmol) according to the general procedure. A trimethyl phosphite reduction of selenoxide was used. The crude product upon purification by preparative TLC using 10/89/1 ether/pentane/NEt_3 gave 0.288 g (82% yield) of the hydroxy selenide as brittle, white crystals: R_f 0.2; mp 108–109 °C; NMR δ 0.88 (s, 9 H), 1.36 (s, 6 H),

1.30-1.70 (m, 7 H), 1.70-1.90 (m, 3 H), 7.16-7.36 (m, 3 H), 7.50-7.70 (m, 2 H); IR (CCl_4) 3500 cm^{-1}.

Anal. Calcd for $C_{19}H_{30}OSe$: C, 64.57; H, 8.56. Found: C, 64.64; H, 8.56.

1-(1-Methyl-1-phenylseleno)ethyl-4-*tert*-butylcyclohexanol (0.349 g, 0.987 mmol) in CH_2Cl_2 was treated with NEt_3 (0.498 g, 0.69 mL, 4.94 mmol) and $MeSO_2Cl$ (0.341 g, 0.23 mL, 2.96 mmol) according to the general procedure.[4] A yield of 0.169 g (94%) of olefin[42] was obtained by short-path distillation (bath 42 °C, 0.072 mm): NMR δ 0.86 (s, 9 H), 1.00-1.80 (m, 7 H), 1.62 (s, 6 H), 2.60-2.80 (m, 2 H).

2,3-Dimethyl-5-phenyl-2-pentene (Table III, Run 5). 2,3-Dimethyl-2-phenylseleno-5-phenyl-3-pentanol was prepared from isopropyl phenyl selenide (3.98 g, 0.020 mol) and 4-phenyl-2-butanone (2.96 g, 0.020 mol) according to the general procedure using a trimethyl phosphite reduction of selenoxide. The crude β-hydroxy selenide was used in the next step without further purification: NMR δ 1.32 (s, 3 H), 1.38 (s, 6 H), 1.69-2.02 (m, 2 H), 2.15 (broad s, 1 H), 2.35-2.93 (m, 2 H), 6.95-7.37 (m, 8 H), 7.49-7.72 (m, 2 H).

The β-hydroxy selenide was converted to the olefin by standard procedures using NEt_3 (10.1 g, 14.0 mL, 0.100 mol) and $MeSO_2Cl$ (6.90 g, 4.65 mL, 0.060 mol). After a typical workup the olefin was separated from 4-phenyl-2-butanone by elution with pentane through a column of silica gel (50 g). The crude olefin (2.41 g) contained a minor amount of Ph_2Se_2. It was purified by Kugelrohr distillation (bath 40-57 °C, 0.072 mm) to give 2.13 g (61% yield) of 2,3-dimethyl-5-phenyl-2-pentene as a clear oil. (A 0.228-g forerun consisting of about 50% of the olefin as well as an unidentified lower molecular weight compound was collected.) NMR: δ 1.53 (s, 3 H), 1.61 (broad s, 6 H), 2.28, 2.59 (AA'BB', 4 H), 7.07 (s, 5 H).

Anal. Calcd for $C_{13}H_{18}$: C, 89.59; H, 10.41. Found: C, 89.40; H, 10.16.

6-Phenyl-2,4-hexadiene (Table III, Run 6). The β-hydroxy selenide was prepared from 2-phenylethyl phenyl selenide (0.261 g, 0.188 mL, 1.0 mmol) and crotonaldehyde (0.070 g, 0.082 mL, 1.0 mmol) according to the general procedure for α-lithio selenoxide additions. After a trimethyl phosphite reduction of selenoxide and typical workup, the crude product was purified by preparative TLC with 20/79/1 ether/hexane/NEt_3 to yield 0.266 g (80% yield) of the β-hydroxy selenide: NMR (mixture of diastereomers) δ 1.64, 1.69 (d, J = 6 Hz, 3 H), 2.26 (broad s, 1 H), 2.69-3.55 (m, 3 H), 4.02 (m, 1 H), 5.31-5.88 (m, 2 H), 7.15 (m, 8 H), 7.34 (m, 2 H); MS M^+ 332.0658 (calcd, 332.0679).

The β-hydroxy selenide was converted to the olefin by treatment with NEt_3 (0.406 g, 0.56 mL, 4.02 mmol) and $MeSO_2Cl$ (0.277 g, 0.19 mL, 2.41 mmol) according to the general procedure[4] for reductive elimination. The crude product was purified by preparative TLC eluting with pentane to give 1.101 g (80% yield) of the diene: R_f 0.3; NMR (E/Z mixture) δ 1.70, 1.78 (d, J = 7 Hz, 3 H), 3.32, 3.44 (d, J = 8, 7 Hz, 2 H), 5.19, 6.54 (m, 4 H), 7.09 (s, 5 H); MS M^+ 158.1092 (calcd, 158.1096).

1-(2-Phenylethylidene)-3,5,5-trimethyl-2-cyclohexene (Table III, Run 7). The β-hydroxy selenide was prepared from 2-phenylethyl phenyl selenide (0.261 g, 0.188 mL, 1.0 mmol) and isophorone (0.138 g, 0.150 mL, 1.0 mmol) according to the general procedure. Purification by preparative TLC eluting twice with 10/89/1 ether/hexane/NEt_3 afforded 0.224 g (56% yield) of the selenide: R_f 0.3; NMR (mixture of diastereomers) δ 1.02, 1.06, 1.09 (s, 6 H), 1.51-1.87 (m, 7 H), 1.87-2.12 (broad s, 1 H), 2.51-2.87 (m, 1 H), 2.92-3.53 (m, 2 H), 5.12, 5.37 (broad s, 1 H), 6.81-7.57 (m, 10 H).

The β-hydroxy selenide was converted to the olefin by treatment with NEt_3 (0.284 g, 0.39 mL, 2.81 mmol) and $MeSO_2Cl$ (0.194 g, 0.13 mL, 1.69 mmol). Purification by preparative TLC, eluting with pentane, afforded 0.066 g (52% yield) of the diene: NMR (E/Z mixture) δ 0.94 (s, 6 H), 1.70, 1.76 (s, 3 H), 1.84 (broad s, 2 H), 1.95, 2.06 (s, 2 H), 3.73, 3.42 (d, J = 7 Hz, 2 H), 5.13-5.32 (broad t, J = 7 Hz, 1 H), 5.75, 6.19 (broad s, 1 H), 7.05 (m, 5 H); MS M^+ 226.1714 (calcd, 226.1722).

Bis(phenylseleno)cyclopropane (24a). To bis(phenylseleno)methane (7.52 g, 23.1 mmol) in 65 mL of THF at −78 °C was added 25.4 mL of 1 M LDA under N_2. After 30 min, ethylene oxide (1.33 g, 1.5 mL, 30.2 mmol) cooled to −78 °C was transferred by cannula to the rapidly stirred solution. The reaction mixture was immediately warmed to 0 °C and reaction allowed to proceed at that temperature for 7 min. At that time, 10 mL of 3 N NH_4OH was poured into the reaction mixture to quench any unreacted starting material. The entire mixture was poured into 20 mL of 10% HCl and 50 mL of 50% ether/hexane. Normal workup gave pure 3,3-bis(phenylseleno)-1-propanol: NMR δ 2.05 (q, J = 7 Hz, 2 H), 3.69 (t, J = 7 Hz, 2 H), 4.59 (t, J = 7 Hz, 1 H), 7.18 (m, 6 H), 7.51 (m, 4 H). The alcohol may be purified by preparative TLC, R_f 0.15, eluting three times with 10% ether/pentane.

Anal. Calcd for $C_{15}H_{16}OSe$: C, 48.65; H, 4.36. Found: C, 48.57; H, 4.36.

The crude selenide was converted to the mesylate **25** according to literature procedure:[43] NMR δ 2.23 (q, J = 7 Hz, 2 H), 2.76 (s, 3 H), 4.30 (t, J = 7 Hz, 2 H), 4.49 (t, J = 7 Hz, 1 H), 7.24 (m, 6 H), 7.53 (m, 4 H).

A 0.645-g portion (assumed to be 1.4 mmol) of the 10.65 g of crude product was taken to prepare the selenide **24a.** A THF solution of **25** was oxidized with MCPBA (0.285 g, 1.4 mmol) at −78 °C and treated with 2.2 mL of 1 M LDA at −78 °C. After 15 min the reaction mixture was treated with NaI/$NaHSO_3$ in the manner described for selenoxide reduction. The crude product was purified by preparative TLC with 10% ether/pentane to give 0.279 g (57% yield) of **24a** as a pale yellow oil: R_f 0.6; NMR δ 1.42 (s, 4 H), 7.16 (m, 6 H), 7.48 (m, 4 H).

Anal. Calcd for $C_{15}H_{14}Se_2$: C, 51.13; H, 4.01. Found: C, 51.12; H, 4.12.

1-Phenylseleno-1-carboxycyclopropane (24d). To 0.45 mL of 1.49 M BuLi in 1.5 mL of THF at − 78 °C was added 1,1-bis(phenylseleno)cyclopropane (**24a,** 0.199 g, 0.565 mmol) in 0.5 mL of THF. The entire mixture was immediately transferred by cannula into 25 mL of solid CO_2. Upon evaporation of excess CO_2, the product mixture was made basic and extracted with 50% ether/pentane to remove butyl phenyl selenide. An NMR spectrum showed about 10% of cyclopropyl phenyl selenide (**24c**). The aqueous phase was acidified with 10% HCl and extracted twice with ether. The combined organic phases were washed with aqueous NaCl, dried over Na_2SO_4, and concentrated at reduced pressure to obtain 0.142 g of a 79:21 mixture of 1-phenylseleno-1-carboxycyclopropane and valeric acid. Crystallization from hexane afforded 0.057 g (42% yield) of **24d** as fine, white needles: mp 72-74 °C; NMR ($CDCl_3$) δ 1.18-1.56 (m, 2 H), 1.56-1.91 (AA'BB', 2 H), 7.12-7.39 (m, 3 H), 7.39-7.65 (m, 2 H), 10.16 (broad s, 1 H).

Anal. Calcd for $C_{10}H_{10}O_2Se$: C, 49.79; H, 4.18. Found: C, 49.75; H, 4.11.

Cyclopropyl Phenyl Selenide (24c). 1,1-Bis(phenylseleno)cyclopropane (**24a**) was treated with *n*-BuLi as above, and the reaction mixture was quenched with water. Separation from butyl phenyl selenide was achieved by preparative gas chromatography (SE-30 on Chromosorb W): NMR δ 1.66 (m, 2 H), 2.0 (m, 2 H), 2.22 (tt, J = 4.5, 7 Hz, 1 H), 7.0-7.5 (m, 5 H); MS M^+ 197.9947 (calcd, 197.9948).

Acknowledgment. We gratefully acknowledge support of this work by the National Science Foundation (Grant CHE 77-15988) and the Wisconsin Alumni Research Foundation. The National Science Foundation also provided funds for the purchase of a mass spectrometer data system (Grant CHE 77-08961). H.J.R. expresses his appreciation to the Du Pont Co. for a Young Faculty Grant and the A. P. Sloan Foundation for a Fellowship. Mr. David Ting assisted in the preparation of a number of selenides.

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Molecular Beam Method for Preparing Stable Solutions of Carbonium Ions

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Abstract: A method is described for carrying out the reaction of SbF_5 and alkyl halides by using deposition of molecular beams of the reagents on a surface cooled to liquid nitrogen temperature to produce stable solutions of carbocations. This procedure is advantageous for preparing ions from unsaturated precursors or when the ions formed can easily isomerize.

Introduction

In 1964, Olah and co-workers[1] described a reaction between SbF_5 and alkyl halides, carried out by mixing solutions of these reagents, which yields carbonium ions (carbocations) as stable solutions where these ions can be examined by using NMR spectroscopy.[2] Since then, numerous publications have appeared concerning structural features,[3] rearrangement rates,[4] and thermodynamic parameters[5,6] in these stable carbocations. The purpose of this paper is to provide a detailed description of an improved technique[7] for carrying out this reaction for preparing stable solutions of carbocations, which we have found to be advantageous over the previously described experimental methods and which we have called the molecular beam method.

Difficulties of Previous Methods. The earlier methods reported work effectively for preparing many carbocations but two serious kinds of difficulty can arise in certain cases. The most common problem results from attempts to ionize unsaturated precursors. Quite often, after the first small amount of ion has been formed from the initial drop of precursor, further addition leads *only* to polymerization, because the addition of carbonium ions to double bonds or other unsaturated groups is an extremely facile reaction step[8] and usually occurs much more rapidly than formation of the desired unsaturated ion. Neither very slow addition nor efficient stirring makes any difference in these cases.

If the ion to be prepared can readily rearrange to a more stable cation, one often finds that an appreciable amount of the rearrangement product has been formed even though the reaction has been run using solutions cooled to a temperature where the desired ion would be stable. We feel that the reason for this is that the ionization reaction is so exothermic that, as each drop of the halide solution is added, local heating occurs which can cause isomerization before the heat is dissipated through stirring.

Very slow addition of a dilute solution with good stirring *can* alleviate this difficulty, but then a dilute solution of the ion is obtained which may not be strong enough to yield a good NMR spectrum. A case where this difficulty arises is the preparation of *sec*-butyl cation from *sec*-butyl chloride where even the use of a dilute solution still resulted in the formation of an appreciable amount of *tert*-butyl cation.[9]

The Molecular Beam Method. Briefly, the present procedure involves transfer of alkyl halides and antimony pentafluoride through separate nozzles into an evacuated chamber where they condense on a liquid-nitrogen-cooled glass surface. SO_2ClF, another solvent, or a substance intended to react with the initially formed cation may be added through a third nozzle in the apparatus if this is desired. The resulting intimate, solid mixture is then dissolved in SO_2ClF at low temperature and transferred to an NMR tube for study.

Scope. The principal advantage of this technique is that the

0002-7863/79/1501-6656$01.00/0