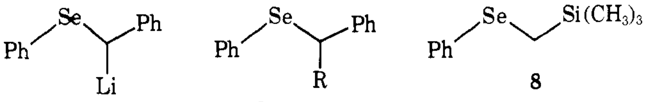
alkylations are rapid at −30°, and are best done at this temperature), the other electrophiles shown react in a few minutes at −78°. No elimination occurs during any of these alkylations. Oxidation, either using the two-phase methylene chloride–hydrogen peroxide procedure,[4b] or by ozonolysis-pyrolysis[10] gives a variety of phenyl substituted olefins. Mitchell[4h] has recently reported the alkylation of **6** by several primary halides, and the oxidation-elimination of the products to give styrenes.

Compounds **7**–**8** are not deprotonated by LDA in THF, but **7b** gives the organolithium with lithium diethylamide (0°, 30 min). The trimethylsilyl substituent is apparently less kinetically acidifying than phenyl, phenylthio, or phenylseleno. The trimethylsilylmethyl selenide **8** is one of the few selenides that can be successfully deprotonated using alkyllithium reagents (*sec*-BuLi–TMEDA in hexane, 90 min, 25°). Only about 15% of cleavage products are obtained. Studies of the use of **7b** and **8** in the synthesis of vinyl silanes and/or carbonyl compounds[16] are in progress.



6

7a, R = CH_3
7b, R = $Si(CH_3)_3$

8

The selenide precursors for the systems **1**–**6** and **8** were prepared by reaction of PhSeNa (from reduction of PhSeSePh with sodium borohydride in ethanol) with the appropriate halide or mesylate, usually at room temperature. Selenides are thus easily prepared, and extension of the methods described here to more complex systems should be limited primarily by compatibility with the oxidizing[17] and deprotonation reagents used. In particular, the method allows the easy transformation of an alkyl halide or alcohol to the functional equivalent of a vinyl anion in reactions with carbonyl compounds.

Acknowledgment. We thank the National Science Foundation, the DuPont Company (DuPont Young Faculty Grant) and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work.

References and Notes

(1) These results were presented in part at the American Chemical Society Midwest Regional Meeting, Iowa City, Iowa, Nov 8, 1974.

(2) (a) D. N. Jones, D. Mundy, and R. D. Whitehouse, *Chem. Commun.*, 86 (1970); (b) K. B. Sharpless, M. W. Young, and R. F. Lauer, *Tetrahedron Lett.*, 1979 (1973).

(3) Synthesis of α,β-unsaturated carbonyl compounds,[4a-f] allylic alcohols,[4e] α,β-unsaturated nitriles,[4f] exomethylene lactones,[4g] and styrenes[4h] have been reported using the selenoxide elimination.

(4) (a) H. J. Reich, I. L. Reich, and J. M. Renga, *J. Am. Chem. Soc.*, **95**, 5813 (1973); (b) H. J. Reich, J. M. Renga, and I. L. Reich, *J. Org. Chem.*, **39**, 2133 (1974); (c) K. B. Sharpless, R. F. Lauer, and A. Y. Teranishi, *J. Am. Chem. Soc.*, **95**, 6137 (1973); (d) D. L. J. Clive, *J. Chem. Soc., Chem. Commun.*, 695 (1973); (e) K. B. Sharpless and R. F. Lauer, *J. Am. Chem. Soc.*, **95**, 2697 (1973); K. B. Sharpless and R. F. Lauer, *J. Org. Chem.*, **39**, 429 (1974); (f) D. N. Brattesani and C. H. Heathcock, *Tetrahedron Lett.*, 2279 (1974); (g) P. A. Grieco and M. Miyashita, *J. Org. Chem.*, **39**, 120 (1974); (h) R. H. Mitchell, *J. Chem. Soc., Chem. Commun.*, 990 (1974).

(5) Only a single direction of elimination (path b) was possible for previous olefin syntheses using lithium reagents derived from α-phenylseleno esters,[4c,g] α-phenylselenino ketones,[4b] α-phenylsulfino esters,[6] and phenyl benzyl selenide.[4h]

(6) B. M. Trost, W. P. Conway, P. E. Strege, and T. J. Dietsche, *J. Am. Chem. Soc.*, **96**, 7165 (1974).

(7) M. Oki and H. Iwamura, *Tetrahedron Lett.*, 2917 (1966).

(8) Ether is used because it is somewhat less rapidly attacked by ozone than is THF. The blue color of excess ozone was used to detect the completion of the oxidation in ether, although the addition of the exact theoretical amount of ozone is preferable. The selenoxide usually precipitates as it is formed but redissolves when LDA is added. Reactions of the anions were usually performed in 1:1 ether–THF.

(9) The oxidation of alkyl phenyl selenides with *m*-chloroperbenzoic acid in THF is complete within 15 min at −10°. Anion formation requires the addition of 2 equiv of LDA.

(10) Sufficient acetic acid is added to neutralize strong base (alkoxide) and protonate half of the amine present, and the cold selenoxide solution is added to refluxing CCl_4 or CH_2Cl_2 under mildly basic conditions (HN-*i*-Pr_2). This procedure gives higher yields of purer products than simply warming the solution to room temperature. The elimination is complete essentially instantaneously in refluxing solvent.

(11) The preparation of α,β-unsaturated nitriles by selenoxide elimination is the only reported case where substantial amounts of cis isomer are formed.[4f]

(12) D. Seebach and N. Peleties, *Angew. Chem.*, **81**, 465 (1969); *Chem. Ber.*, **105**, 511 (1972).

(13) We have found that $PhSeCH_2Li$ can also be prepared from $PhSeCH_2Br$ and *t*-BuLi.

(14) W. Dumont, P. Bayet, and A. Krief, *Angew. Chem., Int. Ed. Engl.*, **13**, 804 (1974); D. Seebach and A. K. Beck, *ibid.*, **13**, 806 (1974). This work, which appeared after submission of our paper, describes the synthesis of allylic alcohols using α-lithio selenides.

(15) H. J. Reich, unpublished results.

(16) The rearrangement of phenyl trimethylsilylmethyl sulfoxide to (phenylthio)(trimethylsiloxy)methane has been reported by A. G. Brook and D. G. Anderson, *Can. J. Chem.*, **46**, 2115 (1968). See also F. A. Carey and O. Hernandez, *J. Org. Chem.*, **38**, 2670 (1973).

(17) G. Ayrey, D. Barnard, and D. T. Woodbridge, *J. Chem. Soc.*, 2089 (1962), have reported that selenides ozonize more rapidly than either 2-methyl-2-pentene or dibutyl sulfide. Ozonolysis of α-phenylseleno ketones[4b] and allyl phenyl selenide[15] occurs selectively at selenium. However, for 3-cyclohexenylmethyl phenyl selenide, *m*-chloroperbenzoic acid is more selective in oxidizing at selenium than ozone.

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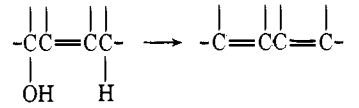
A General Method for the Synthesis of 1,3-Dienes. Simple Syntheses of β- and *trans*-α-Farnesene from Farnesol

Sir:

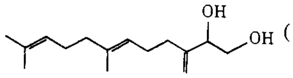
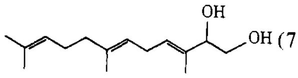
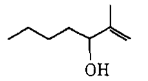
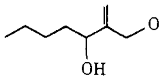
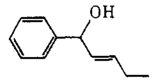
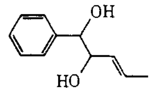
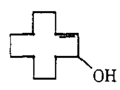
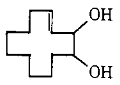
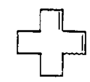
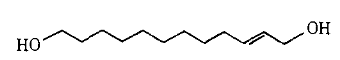
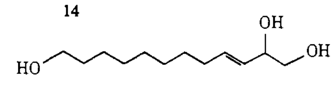
A highly stereospecific transformation of allylic alcohols into ethylenic derivatives has previously been described, as has the application of this reaction to the stereospecific synthesis of C_{18} *Cecropia* juvenile hormone.[1] The process is convenient and depending on the choice of reagent allows the synthesis of either olefinic isomer in good yields with high stereospecificity. We now wish to report a general method for an allylic alcohol → 1,3-diene conversion which depends crucially on the extraordinary effectiveness of organoaluminum reagent in oxirane ring opening.[2] The sequence shown in eq 1, which incorporates this reaction, constitutes a widely applicable method for the generation of 1,3-dienes in very mild conditions.[3]



$$-\underset{\substack{|\\ \mathrm{OH}}}{\overset{|}{\mathrm{C}}}\overset{|}{\mathrm{C}}{=}\overset{|}{\mathrm{C}}\underset{\substack{|\\ \mathrm{H}}}{\overset{|}{\mathrm{C}}}- \longrightarrow -\overset{|}{\mathrm{C}}{=}\overset{|}{\mathrm{C}}\overset{|}{\mathrm{C}}{=}\overset{|}{\mathrm{C}}- \qquad (1)$$

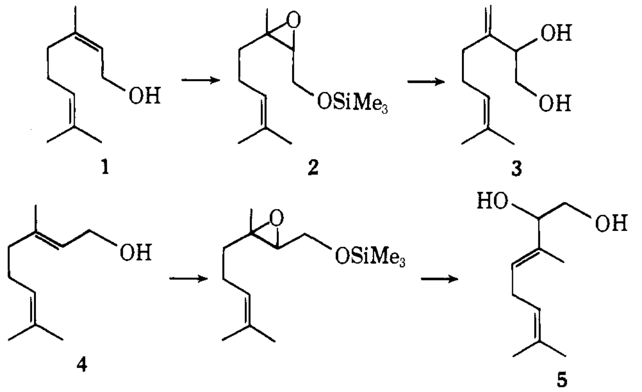
Reaction of nerol (**1**) with vanadium acetylacetonate–*tert*-butyl hydroperoxide in benzene at 25° for 2 hr[1,4] and subsequent treatment of trimethylchlorosilane–hexamethyldisilazane–pyridine at 25° for 30 min produces the epoxy silyl ether **2**. After washing with water and removing of the solvent, the crude product was subjected to the action of diethylaluminum 2,2,6,6-tetramethylpiperidide (DATMP) in benzene at 0° for 2 hr[2] followed by desilylation with excess potassium fluoride in aqueous methanol at 25° for 30 min[5] to produce the 3-substituted 3-butene-1,2-diol **3** (79% based on **1**), homogeneous by TLC and spectroscopically consistent with the indicated structure.[6] An analogous treatment of geraniol (**4**) furnished the isomeric diol **5** in 65% yield;[7] less than 6% of other isomers were determined by chemical degradation into conjugated aldehydes (IO_4^- in ethanol).[8] Thus, in the step of oxirane ring opening, *the site of attack of the organometallic reagent is enforced with remarkable*

Table I. Synthesis of 1,3-Dienes

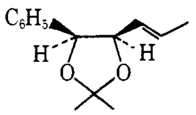
Entry	Starting alcohol	3-Ene-1,2-diol[a] (% yield)[b]	1,3-Diene (% yield)[c]
1	Nerol (1)	3 (79)	8 (58)
2	Geraniol (4)	5 (65)	9 (66)
3	(*Z*, *E*)-Farnesol	 (71)	10 (38)[d]
4	(*E*, *E*)-Farnesol	 (70)	11 (49)[d]
5		 (75)	
6		 (60) 6	
7		 (63) 14	 (70)
8		 (50) 13	12 (75)[g]

[a] All substances have been adequately characterized by analytical and spectral data. [b] Yields refer to pure products after isolation by PLC. [c] Yields refer to pure products after isolation by simple column chromatography (silica gel, hexane as eluant). [d] Zinc powder treatment should be monitored by TLC assay, since the longer reaction time causes the zinc bromide promoted cyclization which diminishes yield of the desired product. [e] A very useful synthetic intermediate for the preparation of substituted trimethylenemethane and other related materials, for which there exist only a limited number of synthetic routes: F. Weiss, *Q. Rev., Chem. Soc.*, 24, 278 (1970). [f] The epoxidation was carried out in toluene at 0° using 2 equiv of *t*-BuOOH. [g] Before the synthesis of diene, the terminal alcohol (C-12) was converted to the acetate. Thus, the treatment of the 1,2,12-triol 13 with 2,2-dimethoxypropane in ether with a catalytic amount of *p*-toluenesulfonic acid at 25° for 30 min followed by acetylation (acetic anhydride–pyridine) afforded the acetonide acetate which was transformed cleanly to the diol using ethylene glycol–tetrahydrofuran and *p*-toluenesulfonic acid as catalyst (89% overall yield).

effectiveness by the presence of the trimethylsiloxy screening group.[9] Further, the stereochemical outcome is fully consistent with the previous observations which can be understood by the rigid stereochemical control introduced by the bulky TMP group.[2]



The generality of the reaction between DATMP and epoxy silyl ether is apparent from the result summarized in Table I. In addition, taken together with the previous observation,[1] it is now possible to prepare 3-butene-1,2-diol derivatives with remarkable stereochemical control. For example, the erythro structure for the diol 6 was demonstrated by the ^{1}H NMR analysis of the corresponding acetonide 7.[10] Thus, the methodology described herein is applicable to a wide variety of synthetic problems in which the stereoselective introduction of 1,2-diol is involved.[11,12]



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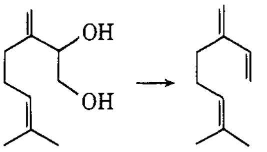
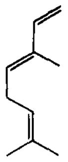
With the demonstration of the high regio- and stereoselectivity for the 3-ene-1,2-diol synthesis, attention was directed toward transformation of the enediol moiety into the 1,3-diene function. Although attempted deoxygenation of 1,2-diol by the procedure of Eastwood[13] gave only a little success (20–30% yield),[14] an alternative route was developed by a sequence of straight-forward steps. Thus, the treatment of the diol 3 with phosphorus tribromide in ether at −78° for 5 min and 0° for 1 hr *in the presence of cuprous bromide* (5 equiv)[15] followed by the addition of excess zinc powder at 0° for 2 hr produced the desired myrcene (8) in 58% yield.[16]



This method accordingly permitted the facile syntheses recorded in Table I of the natural products *trans*-β-ocimene (9),[16] β-, and *trans*-α-farnesene (**10** and **11**, respectively)[16] from their biological precursors. Similarly, the recently isolated sex pheromone **12**, produced by the female red bollworm moth,[17] was synthesized efficiently from the triol **13**, which in turn was prepared from 2-dodecene-1,12-diol. 2-Dodecene-1,12-diol was prepared from the 12-membered diol **14** by sodium metaperiodate oxidation followed by borohydride reduction (73% from **14**).



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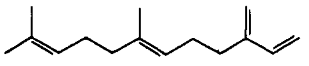

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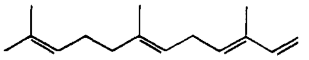

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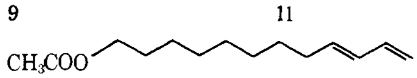


12

References and Notes

(1) S. Tanaka, H. Yamamoto, H. Nozaki, K. B. Sharpless, R. C. Michaelson, and J. D. Cutting, *J. Am. Chem. Soc.*, **96**, 5254 (1974); K. B. Sharpless and R. C. Michaelson, *ibid.*, **95**, 6136 (1973).

(2) A. Yasuda, S. Tanaka, K. Oshima, H. Yamamoto, and H. Nozaki, *J. Am. Chem. Soc.*, **96**, 6513 (1974).

(3) In general, the dehydration of allylic alcohol gives rise to a complex mixture from which the isolation of the desired product is a rather tedious task; see A. Bhati, *Perfum. Essent. Oil Rec.*, **54**, 376 (1963); B. M. Mitzner, S. Lemberg, and E. T. Theimer, *Can. J. Chem.*, **44**, 1090 (1966).

(4) F. List and L. Kuhnen, *Erdoel Kohle*, **20**, 192 (1967); M. N. Sheng and J. G. Zajacek, *J. Org. Chem.*, **35**, 1859 (1970); see also ref 1.

(5) E. J. Corey and A. Venkateswarlu, *J. Am. Chem. Soc.*, **94**, 6190 (1972).

(6) Ir (neat) 3400, 1090, 905 cm^{-1}; ^{1}H NMR ($CDCl_3$, TMS) δ 4.19 (1 H, ABX, C(2)H), 4.97 and 5.14 (2 s, 1 H each, $=CH_2$).

(7) Ir (neat) 3400, 1050, 890 cm^{-1}; ^{1}H NMR ($CDCl_3$, TMS) δ 1.65 (s, 6 H), 1.72 (s, 3 H), 5.12 (t, 1 H, C(6)H), 5.46 (t, 1 H, C(4)H).

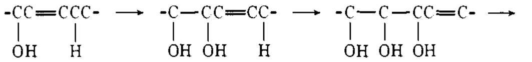
(8) Regio- and stereospecificity of this reaction was easily determined by this technique. ^{1}H NMR (CCl_4, TMS) of CHO δ 9.5 (the aldehyde derived from **3**), 9.3 (the aldehyde derived from **5**), 10.1 (the corresponding *Z* isomer); 1 → **3** 100% regiospecificity and 100% stereospecificity; **4** → **5** 97% regiospecificity and 97% stereospecificity.

(9) None of the vinyl silyl ether was detected in the crude reaction mixture before KF treatment. Even better specificities may be achieved using *tert*-butyldimethylsilyl protecting group (see ref 5) in place of the trimethylsilyl moiety of the epoxy geraniol: 98% regiospecificity and 98% stereospecificity in 92% yield (before KF treatment).

(10) ^{1}H NMR (CCl_4, TMS) of the major isomer (~9:1) δ 4.64 (dd, J = 8 and 6 Hz, C(2)H), 4.85 (dd, J = 8 and 14 Hz, C(3)H), 5.12 (d, J = 6 Hz, C(1)H), 5.49 (dt, J = 14 and 6 Hz, C(4)H); minor isomer δ 4.10 (dd, J = 6 and 9 Hz, C(2)H), 4.63 (d, J = 9 Hz, C(1)H), 5.5–5.7 (complex m, C(3)H and C(4)H).

(11) Only a limited number of synthetic procedures are available for the stereospecific introduction of 1,2-diol unit into carbon skeleton, while such a functional system is frequently contained in many physiologically important substances.

(12) The 3-ene-1,2-diol products can themselves serve as the point of departure for the stereospecific synthesis of polyhydroxy chain systems:



$$\text{-}\underset{\text{OH}}{\text{C}}\text{C}{=}\text{C}\underset{\text{H}}{\text{C}}\text{C-} \longrightarrow \text{-}\underset{\text{OH}}{\text{C}}\text{—}\underset{\text{OH}}{\text{C}}\text{C}{=}\underset{\text{H}}{\text{C}}\text{C-} \longrightarrow \text{-}\underset{\text{OH}}{\text{C}}\text{—}\underset{\text{OH}}{\text{C}}\text{—}\underset{\text{OH}}{\text{C}}\text{C}{=}\text{C-} \longrightarrow$$

(13) F. W. Eastwood, K. J. Harrington, J. S. Josan, and J. L. Pura, *Tetrahedron Lett.*, 5223 (1970).

(14) Other deoxygenation methods from 1,2-diol were also attempted without any success.

(15) The presence of cuprous ion was found to be most essential for this reaction. The detail of this reaction will be published in due course.

(16) Identical in all respects with reported spectrometric data; β-myrcene and *trans*-β-ocimene, G. Ohloff, J. Seibl, and E. Kovats, *Justus Liebigs Ann. Chem.*, **675**, 83 (1964); B. M. Mitzner, E. T. Theimer, L. Steinbach, and J. Wolt, *J. Org. Chem.*, **30**, 646 (1964); β- and *trans*-α-farnesene, K. E. Murray, *Aust. J. Chem.*, **22**, 197 (1969); G. W. K. Cavill, P. J. Williams, and F. B. Whitfield, *Tetrahedron Lett.*, 2201 (1967).

(17) B. F. Nesbitt, P. S. Beevor, R. A. Cole, R. Lester, and R. G. Poppi, *Nature (London), New Biol.*, **244**, 208 (1973); B. F. Nesbitt, P. S. Beevor, R. A. Cole, R. Lester, and R. G. Poppi, *Tetrahedron Lett.*, 4669 (1973); K. Mori, *Tetrahedron*, **30**, 3807 (1974).

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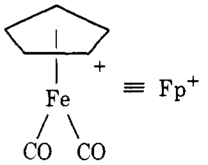
Received January 27, 1975

A Protecting Group for the Carbon–Carbon Double Bond

Sir:

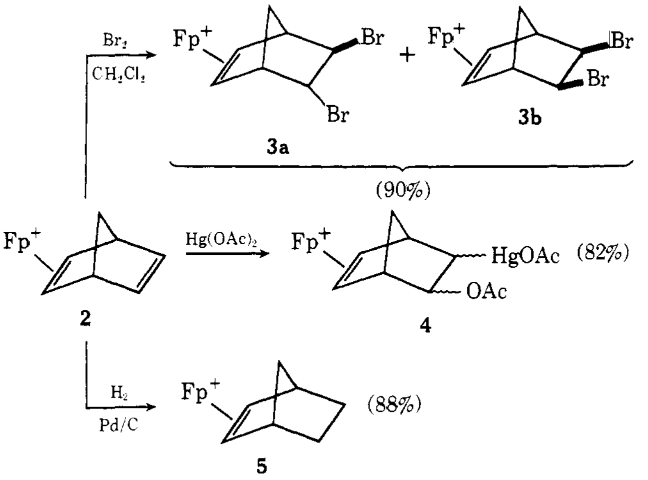
The use of protecting groups plays an important role in organic synthesis. Carbon–carbon unsaturation has mainly been protected by halogenation–dehalogenation and epoxidation–deoxygenation,[1,2] but these methods are limited by competing reactions with other functional groups. We describe herein a practical and selective method of olefin protection which employs the organometallic moiety $C_5H_5Fe(CO)_2^+$ (=Fp^+, below) as the blocking group.



The Fp(olefin)$^+BF_4^-$ complexes may be prepared by several routes[3] the most direct being the thermal exchange reaction between readily available Fp(isobutylene)$^+BF_4^-$ (**1**) and alkenes.[4] The free olefins are conveniently regenerated upon treatment of these complexes with NaI in acetone.[5] We have now found that the coordinated functionality is unreactive toward many reagents which attack carbon–carbon unsaturation thus permitting selective transformations at other reactive centers in polyfunctional alkenes.

Thus, whereas electrophilic (and radical) additions to norbornadiene are frequently accompanied by homoallylic isomerization producting nortricyclane derivatives,[6] Fp(η^2-norbornadiene)$^+BF_4^-$ (**2**), obtained in 74% yield from the exchange reaction,[7,8] smoothly added several electrophiles to the uncoordinated double bond without isomerization (Scheme I). Catalytic hydrogenation of **2** to the norbornene salt **5** (CF_3CO_2H solvent, 25°) was also accomplished. The structures assigned to the products **3a**, **3b**, **4**, and **5** are based upon ir and ^{1}H NMR spectral data and were confirmed by unambiguous synthesis or by characterization of the deprotected ligand.[9] It appears that the free double bond in **2** is somewhat deactivated toward electrophilic attack since methylene chloride solutions of **2** failed to react with HCl, HBr, or *m*-chloroperbenzoic acid at 25° over a few hours.

Scheme I



We have also investigated use of the protecting group with some unsymmetrical polyenes and ene-ynes. The Fp^+ moiety has been found to selectively coordinate to less substituted and/or strained double bonds in several dienes[11] providing a method of protecting these sites which are more reactive toward certain reagents. For example, Fp(4-vinylcyclohexene)$^+BF_4^-$ (**6**) took up 1 equiv of H_2 (10% Pd/C, CF_3CO_2H solvent) to afford Fp(η^2-vinylcyclohexane)$^+BF_4^-$ (**7**, 75%). The *endo*-dicyclopentadiene and 1-octene-4-yne complexes (**8** and **10**) were likewise reduced in good yield to **9** and **11**, respectively. It should be noted here