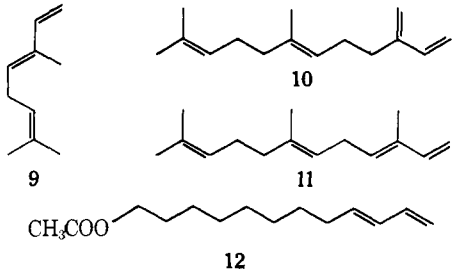

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(1) S. Tanaka, H. Yamamoto, H. Nozaki, K. B. Sharpless, R. C. Michaelson, and J. D. Cutting, *J. Am. Chem. Soc.*, **96**, 5254 (1974); K. B. Sharpless and R. C. Michaelson, *ibid.*, **95**, 6136 (1973).

(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).

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

(6) Ir (neat) 3400, 1090, 905 cm^{-1}; ^1H 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}; ^1H 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).

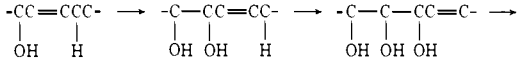
(8) Regio- and stereospecificity of this reaction was easily determined by this technique. ^1H NMR (CCl_4, TMS) of CHO δ 9.5 (the aldehyde derived from **3**), 9.3 (the aldehyde derived from **5**), 10.1 (the corresponding *Z* isomer); **1** → **3** 100% regiospecificity and 100% stereospecificity; **4**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



(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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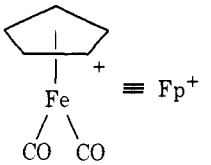
A Protecting Group for the Carbon–Carbon Double Bond

Sir:

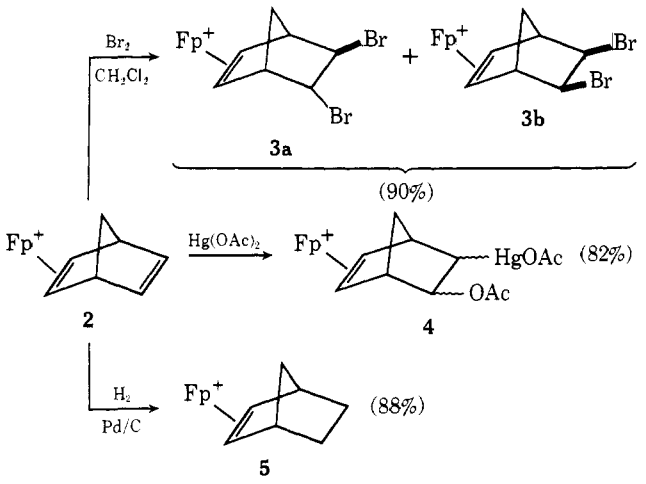
The use of protecting groups plays an important role in organic synthesis. Carbon–carbon unsaturation has mainly been protected by halogenation–dehalogenation and epoxidation–deoxygenation,[1,2] but these methods are limited by competing reactions with other functional groups. We describe herein a practical 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.

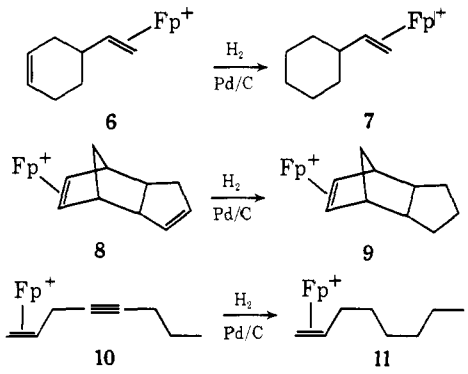
Thus, whereas electrophilic (and radical) additions to norbornadiene are frequently accompanied by homoallylic isomerization producting nortricyclane derivatives,[6] Fp(η^2-norbornadiene)$^+BF_4^-$ (**2**), obtained in 74% yield from the exchange reaction,[7,8] smoothly added several electrophiles to the uncoordinated double bond without isomerization (Scheme I). Catalytic hydrogenation of **2** to the norbornene

Scheme I



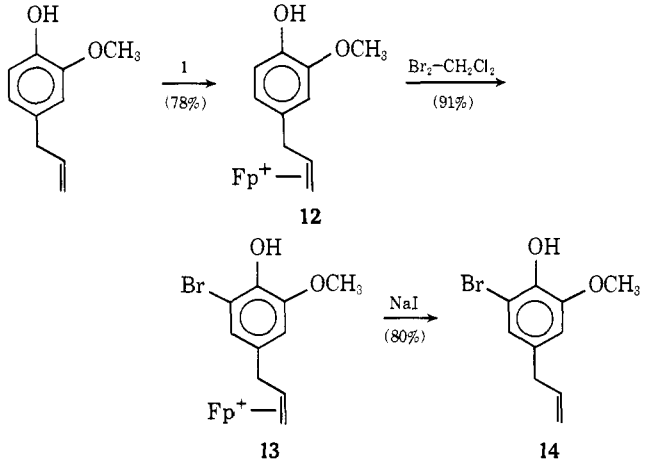
salt **5** (CF_3CO_2H solvent, 25°) was also accomplished. The structures assigned to the products **3a, 3b, 4,** and **5** are based upon ir and ^1H NMR spectral data and were confirmed by unambiguous synthesis or by characterization of the deprotected ligand.[9] It appears that the free double bond 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.

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



that the present protection method complements the more traditional halogenation-dehalogenation procedure since in the latter the protecting group is introduced preferentially at the more substituted double bonds.

Electrophilic addition to the carbon-carbon double bond of olefinic arenes is generally faster than electrophilic aromatic substitution. The latter process may, however, be effected if the substrate is first coordinated to the Fp^+ moiety.[12] For example, whereas bromination of eugenol (Br_2–CH_2Cl_2, 0°) proceeds faster on the olefinic side chain (followed by NMR), aromatic bromination was achieved selectively in good overall yield as shown below. The structure of



14 readily follows from its ^1H NMR spectrum: ($CDCl_3$) δ 7.2 (bs, 1 H, aromatic), 6.75 (bs, 1 H, aromatic), 5.9 (m, 1 H, olefinic), 5.65 (s, 1 H, OH), 5.2–5.0 (m, 2 H, olefinic), 3.9 (s, 3 H, OCH_3), and 3.4 (d, 2H, allylic).[13]

We are currently exploring use of the $C_5H_5Fe(CO)_2^+$ protecting group in the reactions of heterofunctional olefins.

Acknowledgment. Financial support provided by Boston College is gratefully acknowledged.

References and Notes

(1) Review: D. W. Young in "Protective Groups in Organic Chemistry", J. F. McOmie, Ed., Plenum Press, London, Chapter 8.
(2) Several isolated examples of olefin protection which lack general applicability have also been reported, e.g., argentation (G. Subbarao, G. Rao, and K. Achaya, *Tetrahedron Lett.*, 379 (1966)) and alumination (I. E. Levine, German Patent, 1,156,784 (1963)).
(3) Review: M. Rosenblum, *Acc. Chem. Res.*, **7**, 122 (1974).
(4) W. P. Giering and M. Rosenblum, *Chem. Commun.*, 441 (1971).
(5) A. M. Rosan, M. Rosenblum, and J. Tancrede, *J. Am. Chem. Soc.*, **95**, 3062 (1973).
(6) L. Schmerling, J. P. Luvisi, and R. Welch, *J. Am. Chem. Soc.*, **78**, 2819 (1956).
(7) No attempts were made to optimize yields.
(8) Satisfactory elemental analysis were obtained for the complexes **2**, **6**, **8**, **10**, and **13**.
(9) For example, treatment of **3a–3b** with iodide produced a 3:2 mixture of *trans*-:*cis*-*exo*-5,6-dibromonorbornenes determined by comparison of the ^1H NMR spectrum with literature spectra (ref 10). The norbornene salt **5** was identical with that produced from the exchange reaction with norbornene.
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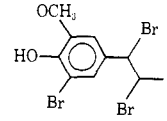
(11) P. F. Boyle and K. M. Nicholas, *J. Org. Chem.*, submitted for publication.
(12) Friedel–Crafts acylations of (diphenylacetylene)$Co_2(CO)_6$ (D. Seyferth and A. Wehman, *J. Am. Chem. Soc.*, **92**, 5520 (1970)) and of (1-phenyl-1,3-butadiene)$Fe(CO)_3$ (R. Pettit and G. F. Emerson, *Adv. Organomet. Chem.*, **1**, 1 (1964)) have been reported.
(13) Bromination of isoeugenol produces



(G. Decodts and M. Wakselman, *Bull. Chem. Soc. Fr.*, 4586 (1972).

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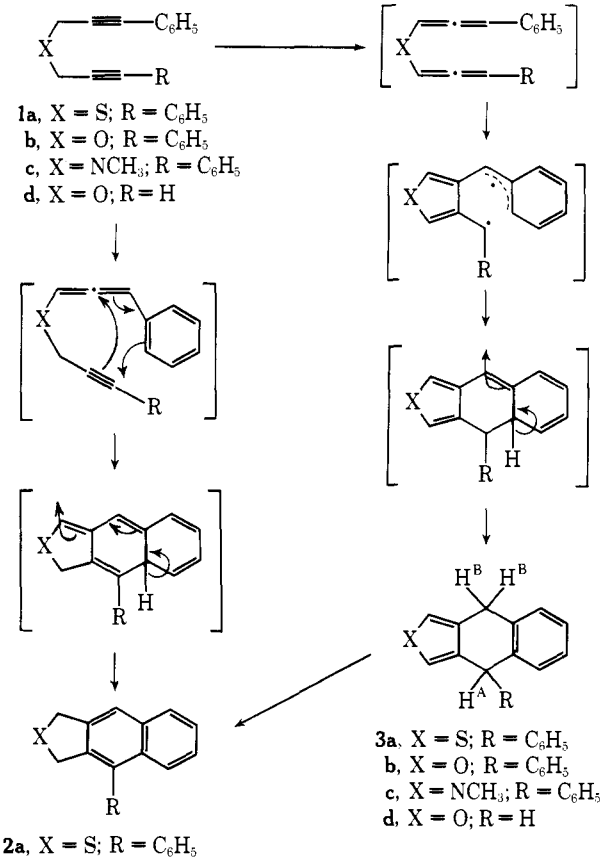
Base Catalyzed Rearrangement of Bispropargyl Sulfides, Ethers, and Amines. The Synthesis of Novel Heterocyclic Systems[1]

Sir:

Over the last 2 decades there has been a renewal of interest in the rearrangement of molecules containing acetylene groups. Both base catalyzed[2] and thermal[3] rearrangements of such systems have been studied and a variety of novel monocyclic,[3] polycyclic,[2,3] and macrocyclic compounds[2b] have been prepared. A smaller number of studies have been

Scheme I



1a, X = S; R = C_6H_5
b, X = O; R = C_6H_5
c, X = NCH_3; R = C_6H_5
d, X = O; R = H

2a, X = S; R = C_6H_5
b, X = O; R = C_6H_5
c, X = NCH_3; R = C_6H_5
d, X = O; R = H

3a, X = S; R = C_6H_5
b, X = O; R = C_6H_5
c, X = NCH_3; R = C_6H_5
d, X = O; R = H