instrument, and chemical shifts are given in parts per million downfield from Me_4Si.

Starting Materials. Commercially available 9-anthraldehyde was purified by column chromatography (SiO_2/CH_2Cl_2). (9-Anthrylmethyl)triphenylphosphonium bromide was prepared according to ref 10. The Lindlar catalyst was purchased from Fluka, AG.

Photochemical Experiments. Actinometric experiments were carried out as described in ref 5. The quantum yield for the cycloaddition of **2** was calculated by subtracting the quantum yield for the cis-trans isomerization from the quantum yield for the disappearance of **2**, both of which are accessible spectrophotometrically. The formation of **3** was ascertained by subsequent irradiation at 280 nm which regenerated **2** from **3** by photolytic cycloreversion but did not affect the yield of **1**. The sensitized formation of **1** from **2** was accomplished by irradiating a benzene solution (7.8×10^{-5} M) and biacetyl (10^{-2} M) in an optical bench arrangement and using a Corning cut-off filter (Type 3-72; $\lambda >$ 430 nm; high-pressue mercury arc, HPK 125 W). The formation of **1** was established and assayed by absorption spectroscopy.

***trans*-1,2-Bis(9-anthryl)ethylene (1).** A solution of lithium ethoxide (prepared from 30 mg of lithium in 28 mL of ethanol) was added to a warm solution of 9-anthraldehyde (0.58 g, 2.8 mmol) and (9-anthrylmethyl)triphenylphosphonium bromide (1.5 g, 2.8 mmol) in absolute ethanol (40 mL). The color of the solution turned transiently red, and yellow crystals precipitated. After the suspension was stirred for 3 h, the precipitate (0.58 g) was removed by filtration, washed with ethanol, and recrystallized from boiling xylene (200 mL): yield 0.48 g (45%) of yellow crystals; mp 350 °C (lit. mp 338,[1] 335 °C[2]); mass spectrum, *m/e* 380 (100, M^+), 378 (10, M - 2), 303 (18, M - 77), 202 (33, M - 178), 190 (7, M - 190), 178 (28, M - 202); M^+ found by high-resolution mass spectroscopy at *m/e* 380.1529, calcd for $C_{30}H_{20}$ *m/e* 380.1566.

***cis*-1,2-Bis(9-anthryl)ethylene (2).** A solution of 1,2-bis(9-anthryl)acetylene[10] (25 mg) in ethyl acetate (150 mL) was hydrogenated under ambient conditions over Lindlar catalyst (1.0 g). After uptake of 1 molar equiv of hydrogen (45 min), the catalyst was removed by filtration, and the solvent was evaporated under reduced pressure. The crystalline residue was recrystallized from CH_2Cl_2 by addition of cyclohexane to give pale yellow crystals: 18 mg (72%); mass spectrum, *m/e* 380 (100, M^+), 378 (12, M - 2), 303 (20, M - 77), 202 (30, M - 178), 190 (12, M - 190), 178 (25, M - 202); M^+ found by high-resolution mass spectrosopy at *m/e* 380.1515, calcd for $C_{30}H_{20}$ *m/e* 380.1566. Anal. Calcd for $C_{30}H_{20}$: C, 94.70; H, 5.30. Found: C, 95.07; H, 5.33. With respect to melting point of **2**, the crystalline appearance of **2** changes around 215 °C, and the substance melts around 348 °C. The thermal formation of **1** was verified by keeping **2** for 3 min at 240-250 °C. The electronic absorption spectrum (in xylene) of the thermolysis product indicated quantitative isomerization of **2** to **1**.

Photochemical Isomerization of 2 To Give 1 and Cycloaddition Product 3. A solution of **2** (30 mg) in cyclohexane (85 mL) was irradiated through Pyrex for 45 min (10 °C; immersion well apparatus; nitrogen atmosphere; high-pressure mercury lamp, HPK 125 W). A yellow crystalline precipitate formed during the irradiation. Vacuum evaporation of the solvent gave a solid yellow residue which was triturated with about 3 mL of $CDCl_3$. Filtration gave 21 mg (70%) of insoluble material which consisted mainly (94%) of trans isomer **1** (determined by absorption spectroscopy). Evaporation of solvent from the $CDCl_3$ filtrate gave a yellow residue which was washed with about 1 mL of CD_3COCD_3 to give 3 mg (10%) of **3** as colorless, needle-shaped crystals. Upon being heated, **3** turns yellow at about 230 °C and melts between 340 and 345 °C: mass spectrum, *m/e* 380 (100, M^+), 378 (22, M - 2), 303 (16, M - 77), 202 (23, M - 178), 191 (13, M - 189), 190 (8, M - 190), 178 (17, M - 202); M^+ found by high-resolution mass spectroscopy at *m/e* 380.1595, calcd for $C_{30}H_{20}$ *m/e* 380.1566.

Acknowledgment. We are indebted to Dr. Kjell Sandros for the actinometric experiments, to Mr. Reine Torberntsson for 270-MHz ^1H NMR spectra, and to Mr. Weston Pimlott for high-resolution mass spectra.

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Dihydrofurans from Hydroxyallenes and Dicarbonyl(η^5-cyclopentadienyl)(η^2-isobutylene)-iron Cation

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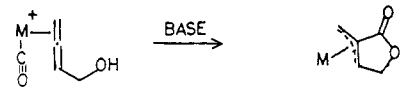
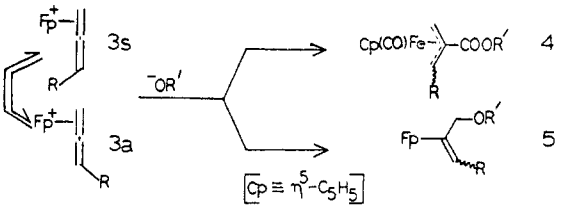
In our studies on the synthetic approaches to functionalized η^3-allyl transition-metal complexes such as **2**,[1] which could be used as versatile intermediates in the synthesis of biologically active lactone-containing natural products, we envisioned a general route through intermediate **1**. Rearrangement of **1** via carbonylation/lactonization might give **2**, in the presence of a suitable base. Such a rearrangement has been recently reported by us[1a] and others[1b] for M = $CpMo(CO)_2$ [Cp ≡ η^5-C_5H_5].



1 2

In the initial stages of the work the analogous iron complex (M = CpFe(CO)) was considered for the **1** to **2** transformation for the following reasons. Fp(η^2-allene) cations without hydroxyl groups [Fp = η^5-$C_5H_5Fe(CO)_2$] are readily prepared via an exchange reaction with the Fp(η^2-isobutylene) cation **8** and a free allene[2] or by protonation of Fp(η^1-propargyl) complex.[3] In addition, certain Fp(η^2-allene) cations (**3**) are known to react with external alkoxides to give carbonylated η^3-allyl complexes **4** and/or products of simple addition to the allene carbon, **5**.[4]



1-Substituted allene complexes exist as syn (**3s**) and anti (**3a**) isomers which slowly interconvert at room temperature.[2] For **1**, which has an internal nucleophile (R = CH_2OH in **3**), it is not clear which mode of attack would predominate. The intermolecular attack of water on Fp(η^2-allene) cations gives only addition to the allene carbon.[5] We report here the results of attempted synthesis of Fp(η^2-hydroxyallene) cations and the chemistry of the observed dihydrofuran products.[6]

(1) (a) Marten, D. F. Paper presented at the 4th Rocky Mountain Regional Meeting of the American Chemical Society, Boulder, CO, June 1978; Abstract No. 167. (b) Benaim, J.; Giulieri, F. *J. Organomet. Chem.* **1979**, *165*, C28-32.

(2) Foxman, B.; Marten, D.; Rosan, A.; Raghu, S.; Rosenblum, M. *J. Am. Chem. Soc.* **1977**, *99*, 2160-5.

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(6) Parts of this work have appeared previously: (a) Marten, D. F. *J. Chem. Soc. Chem. Commun.* **1980**, 341-2; (b) Marten, D. F. Paper presented at the 33rd Southwest Regional Meeting of the American Chemical Society, Dec 1977; Abstract No. 174. (c) Marten, D. F. "Abstracts of Papers", 179th National Meeting of the American Chemical Society, Houston, TX, Mar 1980; American Chemical Society: Washington, DC, 1980; 1980; ORGN 45. Related work has been recently reported: (d) Benaim, J.; L'Honore, A. *J. Organomet. Chem.* **1980**, *202*, C53-7. We thank Professor Benaim for a preprint of this article.

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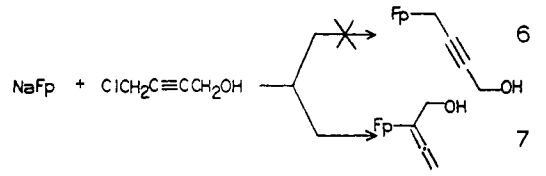
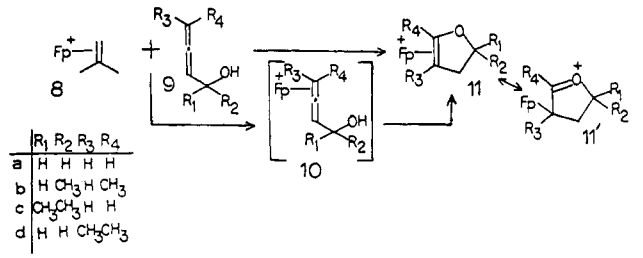
The reaction of 4-chloro-2-butyn-1-ol with NaFp did not yield the expected η^1-propargyl complex **6** but instead gave



the η^1-allenyl isomer **7** in 66% yield. A reasonable explanation for the observed S_N2'-type reaction has previously been presented.[2,5] Compound **7** could not be made to undergo carbonylation/lactonization to produce a structure like **2**.

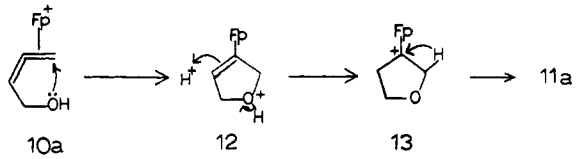
The other approach to Fp(allene) cationic complexes is the exchange reaction of Fp(η^2-isobutylene) cation **8** with the free allene. When **8** was reacted with **9a** under typical



exchange conditions,[3] a yellow solid was obtained in high yield. The product did not have the spectral properties anticipated for the η^2-allene complex **10a**, but the data were consistent with the Fp(η^2-2,3-dihydrofuran) complex **11a**. In the spectral identification of **11a**, two key observations were the low-field ^{1}H NMR absorption (δ 8.37 in CD_3NO_3) of the vinyl proton α to the ether oxygen and the low-energy infrared absorptions (2055 and 2015 cm^{-1}) of the carbonyls. Both of these observations are typical for known[8] vinyl ether complexes and can be explained through the use of resonance form **11a'** which removes positive charge from the metal and places it on the ether oxygen. The ^{13}C NMR was also consistent with this structure. Further proof for structure **11a** was obtained by a decomplexation reaction with NaFp in THF to give the known 2,3-dihydrofuran in 93% yield, identical with 2,3-dihydrofuran obtained from another source.

Intermediate **10a** was implicated through appropriate control experiments. Neither 2,3-dihydrofuran nor 2,5-dihydrofuran yielded **11a** when treated with **8**, indicating rearrangement of the allene did not occur prior to complexation to iron. Isomerization to the acetylene, 3-butyn-1-ol, has also been ruled out, as reported separately.[6a] When 3-butyn-1-ol is reacted with **8**, **11a** is formed along with the Fp(2-oxacyclopentylidene) cation. The absence of the latter complex in the allene reaction with **8** precludes the acetylene being considered as a viable intermediate.

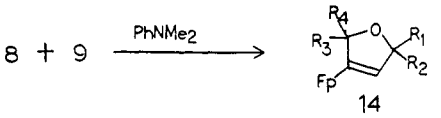
In light of recent results on the hydration of Fp(allene) cations by Klemarczyk and Rosenblum,[5] the mechanism shown below is suggested. Intermediate **10a** is obtained



by exchange with isobutylene. Since the angle about the central allenic carbon is approximately 145°,[8] the hydroxyl oxygen of the CH_2OH group in the more stable anti isomer is in an ideal position to attack the terminal carbon of the complexed allene. The resulting oxonium ion **12** is a strong acid and can protonate the β-carbon of the Fp-vinyl system, generating the carbene complex **13**, which undergoes a hydride shift to give the observed product **11a**. Although it was observed[5] that the anti isomer **3a** (R = CH_3) reacts more slowly toward *external* nucleophiles than the syn isomer **3s** (R = CH_3), which was attributed to steric effects, our example requires the more stable anti geometry, allowing facile *internal* attack by the alcoholic oxygen.

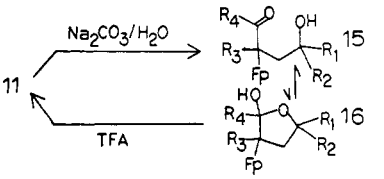
The reaction is not limited to **9a** but also is observed for **9b** which gives complex **11b**. The yield of this reaction is lower (44%), and the product is contaminated with other Fp cations. Attempted exchange with **9c** produced a complex mixture of products, none with a dihydrofuran structure. Analysis of the reaction mixture from **9c** showed no starting allene present after 4 min, but mesityl oxide was present in about 40% yield. Apparently, the strong acid generated under these conditions isomerized the allene to the unsaturated ketone before it could exchange to form the Fp complex.[9] A similar result was obtained with **9d**.

To reduce the acid-catalyzed rearrangement of the allenes, 1 equiv of *N,N*-dimethylaniline was added before the exchange was carried out. Little change was observed in the reaction products for **9a,b** but **9c,d** reacted to form neutral dihydrofuran complexes **14c** and **14d**, respectively.



These products result from direct deprotonation of proposed intermediates similar to **12**. The mode of synthesis was used to assign the structures for **14c** and **14d** since their spectra are almost identical. This is the first example of use of a homogeneous base in the exchange reaction of **8** with olefinic substrates. It is possible that bases could be used with other acid-sensitive materials in an exchange reaction with **8**.[10]

Further evidence for the proposed mechanism of **11** production was obtained by reacting **14c** with trifluoroacetic acid (TFA) and metathesizing with HBF_4 to give the dihydrofuran complex **11c** in 78% yield. These Fp(η^2-



dihydrofuran) cationic complexes are therefore accessible through the two-step procedure of *N,N*-dimethylaniline in the exchange reaction, followed by acid.

$$8 + 9c \xrightarrow[2.\ TFA]{1.\ PhNMe_2/heat} 11c$$

The complexes **11a–c** were readily transformed in high yield to the neutral hydroxy aldehydes and ketone **15** in the presence of Na_2CO_3 and H_2O. It is interesting to note that the ^{1}H NMR and IR spectra of **15a,c** suggest little of the hemiacetal **16** to be present. However, **15c** could easily be converted back to **11c** by brief treatment with

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(8) Foxman, B. M. *J. Chem. Soc., Chem. Commun.* **1975**, *221–2*.
(9) Gelin, R.; Gelin, S.; Albrand, M. *Bull. Soc. Chem. Fr.* **1972**, 720–3.
(10) Use of strongly basic amines (i.e., triethylamine) results in deprotonation of **8** to give Fp(η^1-2-methallyl) prior to exchange.[11]
(11) Rosenblum, M. *Acc. Chem. Res.* **1974**, *7*, 122–8.

TFA. An attempt to make **11d** by reacting **14d** with TFA resulted in an unstable product which could not be fully characterized due to thermal instability. However, the NMR spectrum did show two methyl singlets with chemical shifts consistent with **11d**.[12]

The results presented here indicate that the 1 to 2 transformation will not be possible for the Fp series. The reaction to form the dihydrofuran complexes is faster than carbonyl attack and carbonylation, even in the presence of base ($PhNMe_2$). On possible explanation is that the distance between the complexed carbonyl and the hydroxyl oxygen in the syn complex (**3s**, R = CH_2OH) is too great and prohibits bond formation. We[1a] and others[1b] have found that the η^5-$C_5H_5Mo(CO)_3$ system readily forms an η^3-allyl lactone complex like **2**. The difference between the iron and molybdenum systems may be related to intramolecular distances where the molybdenum is formally seven-coordinate while iron is six-coordinate, placing the reactive groups closer together in the former case.

Experimental Section

Solvents were routinely dried and distilled prior to use. All reactions and workups were carried out under nitrogen.

Infrared spectra were recorded on a Beckman 3750 or a Perkin-Elmer 298. NMR spectra were recorded on a Varian T-60, Varian XL-100, or a Bruker WHX-90. Mass spectra were obtained on a Hewlett-Packard 5985 gas chromatograph–mass spectrometer.

Elemental analyses were performed by Galbraith Laboratories.

Preparation of Allenes. The allenes **9a**,[13] **9b**,[14] **9c**,[9] and **9d**[9] have all been reported previously and were prepared by using standard procedures.[14]

Preparation of 2-Fp-2,3-butadien-1-ol (7). To a flame-dried nitrogen flask was added 4-chloro-2-butyn-1-ol[15] (1.0 g, 9.5 mmol) along with 10 mL of THF. The flask was cooled to −78 °C and NaFp (10 mmol, 0.5 M in THF) added over 5 min via syringe. After 20 more min at −78 °C, the flask was warmed to −25 °C for 2 h and then the solvent evaporated. Filtration through Celite with CH_2Cl_2/ether and recrystallization from ether/hexane yielded **7** as bright yellow needles: 1.55 g (66%); mp 75–76 °C; IR ($CHCl_3$) 2027, 1975 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.88 (s, 5 H, Cp), 4.28 (t, 2 H, J = 4.0 Hz, $=CH_2$), 3.92 (dt, 2 H, J = 4.0, 5.5 Hz, CH_2O), 2.35 (t, 1 H, J = 5.5 Hz, OH); the latter signal disappeared upon addition of D_2O, and the signal at δ 3.92 collapsed to a triplet, J = 4.0 Hz. Anal. Calcd for $C_{11}H_{10}FeO_3$: C, 53.70; H, 4.09. Found: C, 53.45; H, 4.10.

Preparation of Fp(η^2-2,3-dihydrofuran)BF_4 (11a). Isobutylene complex **8** (1.1 g, 3.4 mmol) was suspended in 20 mL of 1,2-dichloroethane containing 2,3-butadiene-1-ol (**9a**; 0.36 g, 5.2 mmol). The mixture was heated at 65 °C for 15 min, and after 5 min a solid formed. The solution was cooled to room temperature ether was added to complete the precipitation, and the solid was collected. The solid was dissolved by using CH_3CN/CH_2Cl_2 (50/50), filtered, and then precipitated with ether to give pure **11a**: 0.949 g (84%); IR (CH_3CN) 2055, 2015 cm^{-1}; ^1H NMR (CD_3NO_2) δ 8.37 (br s, 1 H, H_5), 5.50 (s, 5 H, Cp), 4.73 (dd, 1 H, J = 1.5, 3.6 Hz, H_4), 4.53 (dt, 1 H, J = 2.7, 10 Hz, H_{2t}), 3.60 (ddd, 1 H, J = 8, 10, 11 Hz, H_{2c}), 2.8 (m, 1 H, H_{3t}), 2.3 (m, 1 H, H_{3c}); ^{13}C NMR (CD_3NO_2) δ 212.6 (s, CO), 210.6 (s, CO), 136.1 (d, C_5), 89.6 (d, Cp), 71.6 (t, C_2), 49.0 (d, C_4), 31.1 (t, C_3). Anal. Calcd for $C_{11}H_{11}BF_4FeO_3$: C, 39.57; H, 3.32. Found: C, 39.73; H, 3.34.

Control Reactions of 8 with 2,3-Dihydrofuran and 2,5-Dihydrofuran. When **8** was reacted with 2,3-dihydrofuran or 2,5-dihydrofuran under conditions identical with those for **9a**, none of **11a** could be detected in the product mixture by ^1H NMR.

Reaction of 11a with NaFp. To a flame-dried flask was added NaFp (2.0 mmol, 0.5 M in THF) followed by the dihydrofuran complex **11a** (0.331 g, 1.0 mmol). After 15 min the volatile materials were removed by a water aspirator vacuum and trapped at liquid nitrogen temperature. GC analysis and the ^1H NMR spectrum showed only THF and 2,3-dihydrofuran. The NMR yield of 2,3-dihydrofuran with $CHCl_3$ as an internal standard was 93%. GC collection ($^1/_4$ in. × 10 ft column, 20% TCEP on Chromosorb PAW, 80 °C, flow rate 80 mL/min) yielded pure 2,3-dihydrofuran, which was identical by NMR with an authentic sample.

Preparation of Fp(η^2-2,5-dimethyl-2,3-dihydrofuran)BF_4 (11b). The same reaction procedure as used for **9a** was followed with **8** (0.653 g, 2.04 mmol) and 3,4-hexadien-2-ol (**9b**; 0.300 g, 3.06 mmol) in 15 mL of 1,2-dichloroethane. Upon addition of ether, an oil separated. Ether was decanted, and the residue was dissolved in CH_2Cl_2 and filtered through Celite, and the solvent was removed to give an oil (0.325 g, 44%) of which **11b** was the major component: IR (film) 2055, 2010 cm^{-1}; ^1H NMR (CD_3NO_2) δ 5.43 (s, 5 H, Cp), 4.6 (m, 1 H, H_2), 4.23 (d, 1 H, J = 3.5 Hz, H_4), 2.56 (s, 3 H, C_5 CH_3), 2.53 (d, 1 H, J = 8.0 Hz, H_{3a}), 2.40 (dd, 1 H, J = 3.5 , 8.0 Hz, H_{3b}), 1.51 (d, 3 H, J = 6.0 Hz, C_2 CH_3). Since the isolated product was a mixture as indicted by extra signals in the NMR, an analysis was not obtained. However **11b** was converted to **15b** which did provide a good analysis (see below).

Attempted Formation of Fp(η^2-2,2-dimethyl-2,3-dihydrofuran)BF_4 (11c). The reaction of **8** with 2-methyl-3,4-pentadien-2-ol (**9c**) yielded a mixture of Fp cations, none of which could be conclusively identified as **11c**. GC analysis of the reaction mixture after 4 min showed no starting allene to be present, but mestyl oxide, in 40% yield, was identified by GC/MS.

Synthesis of 4-Fp-2,25-dimethyl-2,5-dihydrofuran (14c) Using $PhNMe_2$. To a side-arm 100-mL flask were added **8** (0.666 g, 2.08 mmol), **9c** (0.413 g, 4.2 mmol), and *N,N*-dimethylaniline (0.281 g, 2.32 mmol) along with 15 mL 1,2-dichloroethane. After being heated at 65 °C for 20 min, the reaction was cooled, diluted with ether, and filtered through alumina (activity III, neutral), and the solvent was removed. The residue was chromatographed on alumina (activity III, neutral), producing a yellow band, after elution of Fp_2 with 20/80 ether/hexane, which was identified as **14c**: 0.297 g (52%); mp 56–57 °C; IR (KBr) 2010, 1955 cm^{-1}; ^1H NMR (CS_2) δ 5.23 (t, 1 H, J = 2.0 Hz, H_3), 4.74 (s, 5 H, Cp), 4.22 (d, 2 H, J = 2.0 Hz, H_5), 1.08 (s, 6 H, CH_3's). Anal. Calcd for $C_{13}H_{14}FeO_3$: C, 57.01; H, 5.07. Found: C, 57.38; H, 5.30.

Synthesis of 3-Fp-2,2-dimethyl-2,5-dihydrofuran (14d). The same procedure as used for **14c** was followed with **8** (0.323 g, 1.01 mmol), 4-methyl-2,3-pentadien-1-ol (**9d**; 0.196 g, 2.0 mmol), and *N,N*-dimethylaniline (0.145 g, 1,3 mmol). After chromatography, the crude material (0.195 g, 71%) was sublimed at 0.1 mm to yield analytically pure **14d**: 0.169 g (62%), mp 62–64 °C; IR (KBr) 2010, 1955 cm^{-1}; ^1H NMR (CS_2) 5.20 (t, 1 H, J = 1.6 Hz, H_4) 4.77 (s, 5 H, Cp), 4.24 (d, 2 H, J = 1.6 Hz, H_5), 1.12 (s, 6 H, CH_3's). Anal. Calcd for $C_{13}H_{14}FeO_3$: C, 57.01; H, 5.07. Found: C, 57.01; H, 5.01.

Synthesis of Fp(η^2-2,2-dimethyl-2,3-dihydrofuran)BF_4 (11c) from 14c. The product **14c** (0.197 g, 0.72 mmol) was dissolved in 5 mL of nitromethane and cooled to 0 °C. Trifluoroacetic acid (0.236 g, 2.0 mmol) was added followed by 48% tetrafluoroboric acid (0.323 g, 1.8 mmol). Addition of ether yielded a yellow solid identified as **11c**: 0.204 g (78%); IR (KBr) 2045, 2005 cm^{-1}; ^1H NMR (CD_3NO_2) δ 8.36 (br s, 1 H, H_5), 5.51 (s, 5 H, Cp), 4.88 (br d, 1 H, J = 5.5 Hz, H_4), 2.7 (dd, 1 H, J = 5.5, 16.0 Hz, H_{3a}), 2.3 (br d, 1 H, J = 16.0 Hz, H_{3b}), 1.40 (s, 3 H, CH_{3a}) 1.30 (s, 3 H, CH_{3b}). Anal. Calcd for $C_{13}H_{15}BF_4FeO_3$: C, 43.14; H, 4.18. Found: C, 42.95; H, 4.35.

Preparation of 2-Fp-4-hydroxybutanal (15a) from 11a. A sample of **11a** (0.371 g, 1.11 mmol) was dissolved in 5 mL of CH_3CN and 5 mL of 10% Na_2CO_3 in water added. After 5 min at room temperature ether was added, the layers were separated, the ether layer was dried with $MgSO_4$ and filtered, and the solvent was removed. Chromatography of the residue on silica gel showed a bright yellow band which was eluted with CH_3CN/CH_3OH (90/10) to give **15a** as a yellow solid, 0.205 g (70%). Recrystallization yielded analytically pure material: 0.163 g (56%): mp 98–99 °C; IR (KBr) 3400, 2015, 1960, 1625 cm^{-1}; ^1H NMR ($CDCl_3$) δ 9.28 (d, 1 H, J = 2.0 Hz, H_1), 4.78 (s, 5 H, Cp), 3.6 (m, 2 H, H_4),

(12) It is also possible that this product is the elusive η^2-allene complex. The apparent instability of the observed product warrants against this possibility, however.

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1.6–2.5 (m, 4 H, H_2, H_3, OH). Anal. Calcd for $C_{11}H_{12}FeO_4$: C, 50.03; H, 4.58. Found: C, 49.70; H, 4.69.

Preparation of 3-Fp-5-hydroxy-2-pentanone (15b). The reaction of **8** (0.653 g, 2.04 mmol) with **9b** (0.316 g, 3.24 mmol) in the presence of $PhNMe_2$ (0.258 g, 2.13 mmol) gave no detectable **14b**. The product was directly reacted with 10 mL of 10% Na_2CO_3 with THF as a cosolvent. Chromatography on alumina (activity III, neutral) yielded **15b** upon elution with CH_3CN/CH_3OH (10/1); 0.200 g (34%). Recrystallization from CH_2Cl_2/hexane gave an analyticlaly pure solid, mp 93–94 °C. The crude material showed a mixture of diastereomers in the ^1H NMR spectrum (3:1). The reported NMR is for the major component: IR (film) 3500, 2010, 1970, 1630 cm^{-1}; ^1H NMR ($CDCl_3$) 4.77 (s, 5 H, Cp), 3.7 (m, 1 H, H_5), 2.80 (dd, 1 H, J = 2.0, 11.0 Hz, H_3), 2.22 (ddd, 1 H, J = 3.0, 11.0, 14.0 Hz, H_{4a}), 2.16 (s, 3 H, H_1), 1.49 (ddd, 1 H, J = 2.0, 8.0, 14.0 Hz, H_{4b}), 1.13 (d, 3 H, J = 6.0 Hz, H_6), the position of the OH signal was not determined. Anal. Calcd for $C_{13}H_{16}FeO_4$: C, 53.45; H, 5.52. Found: C, 53.44; H, 5.70.

Preparation of 2-Fp-4-hydroxy-4-methylpentanal (15c). Complex **11c** (0.118 g, 0.326 mmol) was reacted with Na_2CO_3 as with **15a** to yield **15c**: 0.097 g (100%), mp 94–95 °C dec; IR ($CDCl_3$) 2015, 1945, 1630 cm^{-1}; ^1H NMR (CD_3NO_2) δ 9.19 (d, 1 H, J = 3.2, H_1), 4.92 (s, 5 H, Cp), 2.72 (ddd, 1 H, J = 2.0, 3.2, 11.0 Hz, H_2), 2.30 (dd, 1 H, J = 11.0, 14.0 Hz, H_{3a}), 1.62 (dd, 1 H, J = 2.0, 14.0 Hz, H_{3b}), 1.09 (s, 6 H, CH_3's), 2.48 (s, 1 H, OH). Anal. Calcd. for $C_{13}H_{16}FeO_4$: C, 53.45, H, 5.52. Found: C, 53.42, 5.62. An NMR experiment in CO_3NO_2 showed that **15c** could be cleanly transformed back to **11c** by using trifluoroacetic acid.

Attempted Preparation of 11d. Compound **14d** (30 mg) was dissolved in CD_3NO_2 and filtered through Celite into an NMR tube. Upon addition of 10 μL of trifluoroacetic acid, new signals appeared as singlets at δ 5.37, 2.50, and 1.80. After 3 h at room temperature, the signals for **14d** and the new product had disappeared and were replaced by a singlet at δ 5.25. The rest of the spectrum was very broad.

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Registry No. 7, 76983-90-9; 8, 46238-51-1; **9a**, 18913-31-0; **9b**, 40296-27-3; **9c**, 34761-53-0; **9d**, 2425-45-8; **11a**, 76983-93-2; **11b**, 79391-83-6; **11c**, 79391-85-8; **14c**, 79391-86-9; **14d**, 79391-87-0; **15a**, 79391-88-1; **15b**, 79391-89-2; **15c**, 79391-90-5; NaF_p, 12152-20-4; 4-chloro-2-butyn-1-ol, 13280-07-4.

Benzenesulfonylcarbonitrile Oxide. 3. Useful New Procedures for Generation

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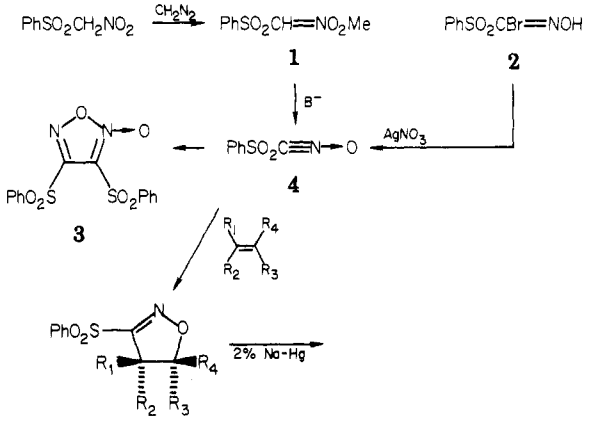
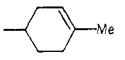
Chemoselective processes permitting the functionalization of isolated carbon–carbon double bonds are currently of major synthetic importance, and this importance continues to grow in concert with the development of improved methods for the preparation of alkenes. Nitrile oxides cycloadd to alkenes in one such process, many diverse functionalities being tolerated in the reacting partners. This, in conjunction with straightforward transformation procedures, has led to a number of useful new synthetic procedures.[1]

Scheme I

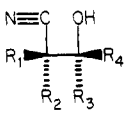


5a, $R_1 = R_2 = R_3 = H$; $R_4 = n$-Bu

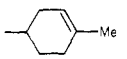
b, $R_1 = R_2 = H$; $R_3 = Me$; R_4 = 

c, $R_1 = H$; $R_2R_3 = -(CH_2)_4-$; $R_4 = Me$

d, $R_1 = R_2 = R_3 = R_4 = Me$



6a, $R_1 = R_2 = R_3 = H$; $R_4 = n$-Bu

b, $R_1 = R_2 = H$; $R_3 = Me$; R_4 = 

c, $R_2 = R_3 = H$; R_1R_4 = 

We have recently reported the use of benzenesulfonylcarbonitrile oxide (**4**) in the functionalization of alkenes.[2] For simple alkenes two limitations were encountered. Reaction with 2,3-dimethyl-2-butene gave only a 17% yield of cycloadduct, even with a large excess of the alkene. Also, the required precursor to nitrile oxide **4** involved a four-step preparation. Here we report two new procedures for generating this nitrile oxide each of which eliminates one of these problems.

The methyl nitronic ester **1** provides easy access to nitrile oxide **4**.[3] (Phenylsulfonyl)nitromethane is O-methylated with diazomethane and the derived crude **1** treated with aqueous sodium silicate or hydroxide in a two-phase system (Scheme I). In the absence of alkene, nitrile oxide dimer **3** is obtained in 44% yield, indicating some side reactions to the formation of the 1,3-dipole. However, when an excess of reagents is employed in the

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