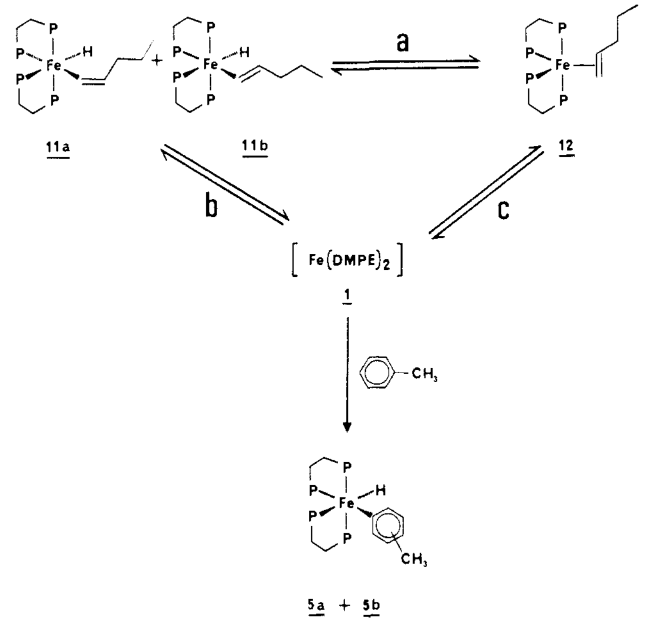
Scheme II



Treatment of a reaction mixture containing the vinyl hydride **9** with $CHCl_3$[13] afforded the thermally stable derivative *trans*-$ClFe(CH{=}CH_2)(DMPE)_2$ (**13**), while treatment with CH_2Br_2 afforded *trans*-$BrFe(CH{=}CH_2)(DMPE)_2$ (**14**). Similarly, treatment of a mixture of the cyclopentenyl iron hydrides **7** and **8** with CH_2Br_2 afforded the corresponding bromide, *trans*-$BrFe(\overline{C{=}CHCH_2CH_2CH_2})(DMPE)_2$ (**15**). We have evidence that the *cis*-alkenyl iron hydrides react with $CHCl_3$ or CH_2Br_2 to form *cis*-halo derivatives initially, and these isomerize to the trans complexes on warming. After they were quenched with the haloalkanes, the reaction mixtures always contained *trans*-$Br_2Fe(DMPE)_2$ or *trans*-$Cl_2Fe(DMPE)_2$[14] in varying amounts.

The π-complex **12** is fluxional on the NMR time scale at room temperature, but this is not unexpected as the analogous π-complexes of ethylene, propylene, 1-butene, and styrene also exhibit dynamic behavior on the NMR time scale.[5a] **12** is photochemically labile, and photolysis at −80 °C in the presence of excess 1-pentene leads to the reformation of a mixture which contains **11a** and **11b** as dominant products. In a sealed tube, the cycle **11a** + **11b** (warm) $\rightarrow$ **12** ($h\nu$, −80 °C) $\rightarrow$ **11a** + **11b** was repeated 6 times with no significant degradation of the sample.

Irradiation of either **12** or a mixture of **11a** and **11b** at −80 °C in the presence of toluene led to formation of the tolyl iron hydrides **5a** and **5b**. This suggests that, under photolytic conditions, each of the complexes **11a**, **11b**, and **12** affords the coordinatively unsaturated intermediate **1** which reacts with the added arene. In Scheme II, at least two of the three pathways a, b, or c must operate under photochemical conditions. At present, we have no evidence to indicate whether **12** is an intermediate in the conversion of **11a** and **11b** to **1** or vice versa.[15]

Acknowledgment. We gratefully acknowledge financial support from the Australian Research Grants Scheme and the Australian Government for a Commonwealth Postgraduate Award (M.V.B.).

Supplementary Material Available: ^1H and ^{31}P NMR spectral data for compounds **3**–**15** (4 pages). Ordering information is given on any current masthead page.

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[13] In a typical experiment, 2–4 equiv of a solution of $CHCl_3$ or CH_2Br_2 (0.2 M in pentane) was added to a sample of an alkenyl iron hydride in pentane at −78 °C. The sample was warmed to room temperature, stripped of solvent under vacuum, and extracted into deuteriobenzene.

[14] Chatt, J.; Hayter, R. G. *J. Chem. Soc.* **1961**, 5507–5511.

[15] The coordinatively unsaturated intermediate $Fe(DEPE)_2$ [DEPE = 1,2-bis(diethylphosphino)ethane], an analogue of **1**, reacts with C–H bonds in ethylene *without* prior formation of the π-complex. Baker, M. V.; Field, L. D. *J. Am. Chem. Soc.*, in press.

Conformer Selection by Monolayer Compression

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Cyclization of nerol (**1a**) and its derivatives is a well-known reaction in terpene chemistry. Zeitschel[1] proved the cis configuration for nerol by showing that it cyclizes to α-terpineol (**4**), 9 times faster than geraniol (**2**) in dilute sulfuric acid. Several kinetic studies have shown that neryl derivatives solvolyze with π-participation of the remote double bond.[2-7] This participation imposes considerable restraints upon the transition state in terms of partial gauche butane-like interactions and a loss of rotational entropy estimated to be ca. 5.5 eu,[6] leading to only modest rate enhancements relative to the geranyl isomers which react to give largely acyclic products.

In the present study the ability of nerol and geraniol to form monolayers as a consequence of their amphipathic nature has been exploited to select conformers. In the monolayer the OH group is incorporated into the aqueous subphase and the hydrocarbon chain oriented away from it. When the monolayer is compressed to a high surface pressure, the hydrocarbon chains are forced out into a vertical position, while at low surface pressures the monolayer is in an expanded state, the hydrophobic chains are less oriented, and the molecules lie randomly on the surface. This difference has been used to select conformers of compressed and expanded films over dilute sulfuric acid, using a modified Langmuir trough consisting of a thermostated multicompartmental PTFE trough with a Wilhelmy plate balance.[8] The subphases (in this case 5% H_2SO_4 and water) could be confined in different compartments and the monolayers transferred from one to the other with minimal mixing. In a typical experiment 100 μL of a 0.1 M solution of the alcohol in hexane was spread on water, compressed to over 20 dyn cm^{-1} and transferred to 5% H_2SO_4 at 25 °C. After 5 min the layer was transferred to water, the monolayer material extracted into hexane, and the products determined by GLC. For the expanded films the monolayer was spread directly over the acid and allowed to react for 5 min. Since the surface pressures were as low as 2 dyn cm^{-1}, the films were compressed before transfer over water and extraction.[10]

Compressed nerol films remain largely unreacted giving <5% α-terpineol. By contrast expanded films with the same exposure time gave >90% cyclization to α-terpineol and <10% nerol. Clearly in compressed films existence of conformers **1b** leading to **1c** (Scheme I) is strongly disfavored and the monolayer may be considered to consist largely of extended conformers of the type **1a**. With expanded films conformer **1b** is accessible, despite being at least 1.5 kcal higher in energy than the extended conformers,[6] and may be stabilized by hydrophilic interaction of the remote double bond with the aqueous subphase.[9] Formation of transition state **1c** is thereby strongly favored. Interestingly <2% linalol (**3**) is formed in either film, and this points to negligible "slipping" of extended conformers to the allylically delocalized cation in the compressed films. In expanded films the factors favoring reaction of conformer **1b** to cyclic products seem overwhelming, in contrast to the behavior of neryl cations in bulk-phase hydrolyses where

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[1] Zeitschel, O. *Ber. Dtsch. Ges.* **1906**, *39*, 1780.

[2] Valenzuela, P.; Cori, O. *Tetrahedron Lett.* **1967**, 3089.

[3] Cramer, F.; Rittersdorf, W. *Tetrahedron* **1967**, *23*, 3015.

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[6] Astin, K. B.; Whiting, M. C. *J. Chem. Soc., Perkin Trans. 2* **1976**, 1160.

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[8] Fromherz, P. *Rev. Sci. Instrum.* **1975**, *46*, 1380.

[9] E.g.: Davies, J. T.; Rideal, E. K. *Interfacial Phenomena*; Academic Press: New York, 1963; p 284.

[10] In view of the low alcohol concentrations required for the monolayer studies, overall yields could not be reliably assessed. However, reaction times were maintained strictly constant and our conclusions regarding relative reactivities of the conformers retain their validity.

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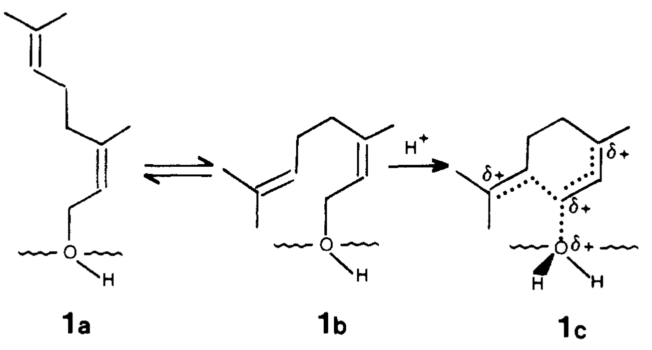
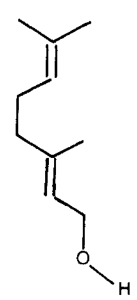
Scheme I

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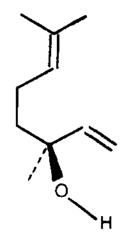
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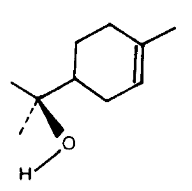
4

ca. 10–20% of linalol is obtained.[2,3,7]

Compressed geraniol films are similarly unreactive, again giving <5% reaction. Expanded films gave ~70% linalol, ~10% α-terpineol, and ~20% geraniol. Here the reaction more closely parallels behavior of geranyl cations in aqueous media,[2,3,7] where linalol is also the major substitution product, suggesting the facile formation of the allylic cation in the expanded film.

Crossover products, i.e., geraniol from nerol films and nerol from geraniol films, are small (<2%) and attest to the geometrical integrity of the cations produced.

Carbenoids. Metal-Assisted Ionization[1]

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Received July 8, 1986

Ordinarily vinyl and cyclopropyl halides are extremely slow to ionize. However, in those systems where the carbon atom bearing the halogen also contains a lithium atom, the halogen is removed as an anion extremely rapidly even at temperatures as low as −100 to −50 °C and in solvents such as ether and tetrahydrofuran. We have recently[3,4] provided evidence that these carbenoids (carbon atoms possessing both an halogen and a metal) are best viewed as cationic intermediates in which the metal (lithium) is coordinating with and assisting in the ionization of the halogen (leaving group) and thereby forming a carbon cation–halogen anion tight ion pair (**2**). We have referred to this coordination of the halogen by the metal as metal-assisted ionization (MAI). The stereochemical result observed in the reaction of **2** is similar to that observed in general for the $\mathrm{S_N}^1$ type of reactions of chiral halides: some racemization with overall inversion of configuration.[3,4] Thus in the reactions of (*S*)-(+)-**1** (X = Cl) with *tert*-butyllithium in ether at −75 °C, (*R*)-(−)-**3** is formed with an optical purity of 31% and with overall inversion of configuration.

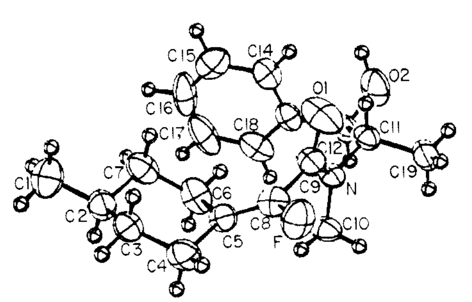
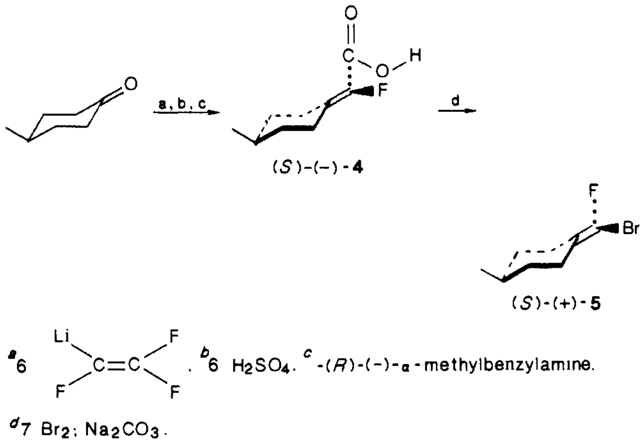
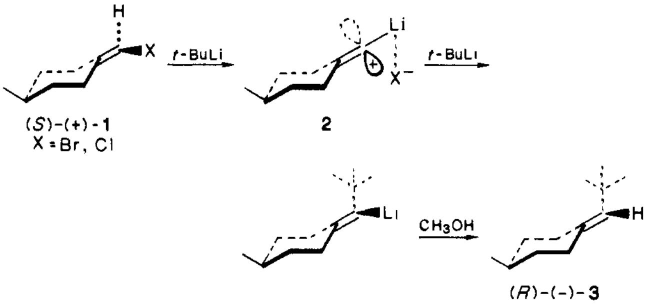


Figure 1. ORTEP plot of *N*-(*S*)-(−)-(4-methylcyclohexylidene)fluoroacetyl-L-(−)-ephedrine.

Scheme I



^{a}6 · ^{b}6 H_2SO_4. ^{c}-(*R*)-(−)-α-methylbenzylamine. ^{d}7 Br_2; Na_2CO_3.



Since it has been shown the fluorides solvolyze roughly 10^6–10^7 slower than chlorides, it was of interest to determine whether MAI would still be operative when X = F in **1**.

Scheme I describes the preparation of the system **5** which was selected for investigation so that the halogen metal exchange reactions could be used to generate the carbenoid, rather than metalation as we had previously employed.[3,4] The former reaction also permits one to generate the carbenoid at lower temperatures. The synthesis of **5**, $[\alpha]^{22}_{\mathrm{Hg}}$ +11.9° (*c* 1.1, C_2H_5OH) is straightforward and was accomplished by the brominative decarboxylation of **4**, $[\alpha]^{22}_{\mathrm{Hg}}$ −41.3 (*c* 1.1, C_2H_5OH), a reaction shown to be stereospecific in the cyclohexylidene series.[7] The absolute configuration of (−)-**4** was established as *S* from the X-ray crystal structure analysis of the amide formed from (−)-**4** and L-(−)-ephedrine (Figure 1). Since brominative decarboxylation leads to inverted product,[7] (+)-**5** has the *S* configuration.

Treatment of (*S*)-(+)-**5** with 3 equiv of *tert*-butyllithium in ether solvent at -100 °C for 5 min, followed by protonolysis with methanol, gave a 40% yield of (*S*)-(−)-**3**, $[\alpha]^{22}_{\mathrm{Hg}}$ −9.7° (*c* 1,1,

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[1] This work was supported by a grant (CHE-8503227) from the National Science Foundation. A NATO Travel Grant (741/84) to one of us (H.M.W.) is also appreciated.

[2] Visiting Professor from the Institute of Organic Chemistry, Technical University, Gdansk, Poland.

[3] Duraisamy, M.; Walborsky, H. M. *J. Am. Chem. Soc.* **1984**, *106*, 5035.

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