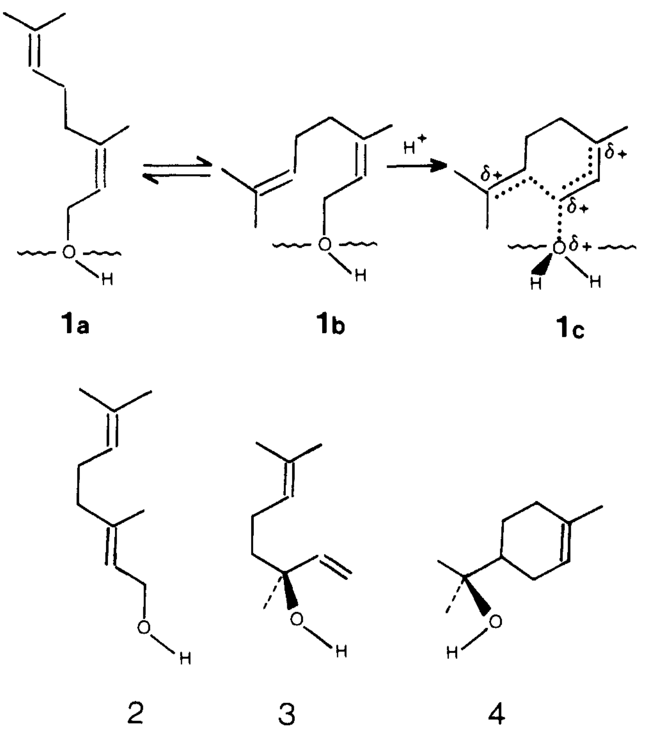
Scheme I



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]

Janusz Rachon,[2] V. Goedken, and H. M. Walborsky*

Department of Chemistry, Florida State University
Tallahassee, Florida 32306-3006

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 $S_N{}^1$ 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.

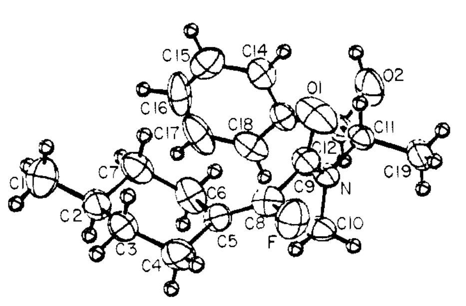
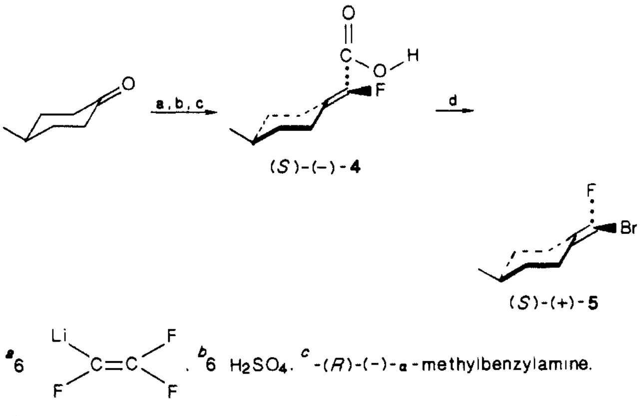
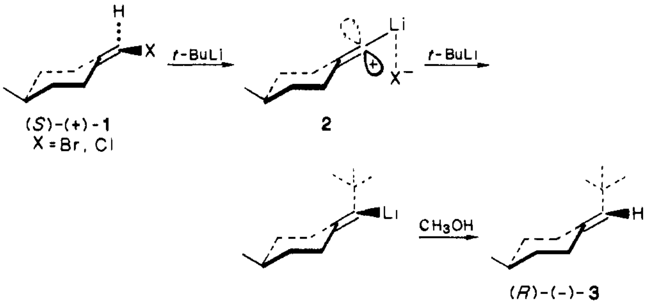


Figure 1. ORTEP plot of *N*-(*S*)-(−)-(4-methylcyclohexylidene)fluoroacetyl-L-(−)-ephedrine.

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**, $[\alpha]^{22}_{Hg}$ +11.9° (*c* 1.1, C_2H_5OH) is straightforward and was accomplished by the brominative decarboxylation of **4**, $[\alpha]^{22}_{Hg}$ −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**, $[\alpha]^{22}_{Hg}$ −9.7° (*c* 1,1,

---

[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.

[4] Walborsky, H. M.; Duraisamy, M. *Tetrahedron Lett.* **1985**, *26*, 2743.

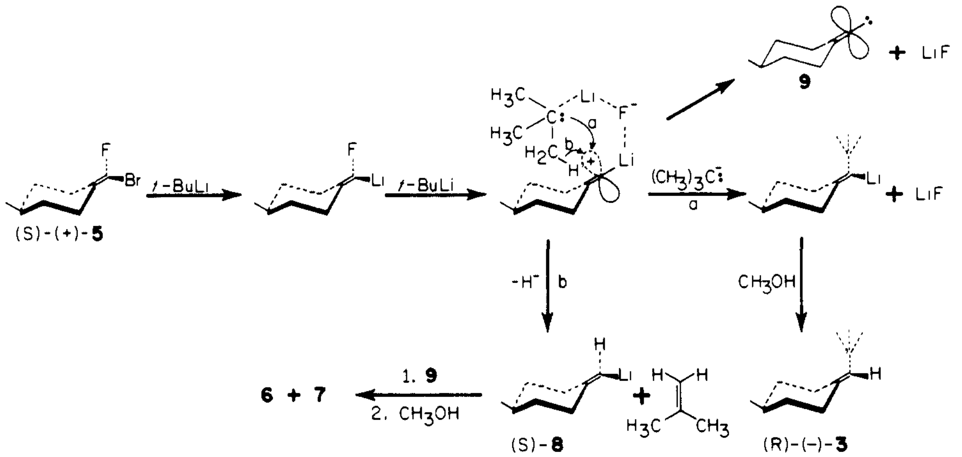
[5] Noyce, D. S.; Vigilio, J. A. *J. Org. Chem.* **1972**, *37*, 2643.

[6] Normant, J. F.; Foulon, J. P.; Masure, D.; Sauvetre, R.; Villiers, J. *Synthesis* **1975**, 122.

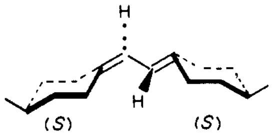
[7] Walborsky, H. M.; Banks, R. B. *Bull. Soc. Chem. Belg.* **1980**, *89*, 849.

0002-7863/86/1508-7435$01.50/0

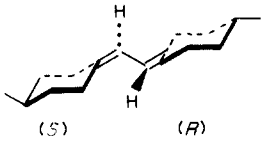
Scheme II



$CHCl_3$) and a 30% yield of (−)-1,2-bis(4-methylcyclohexylidene)ethane, $[\alpha]^{22}_{\mathrm{Hg}}$ −10.9° (c 1.0, C_2H_5OH). The latter was shown by NMR to be a 1:1 mixture of chiral **6** and meso **7**.

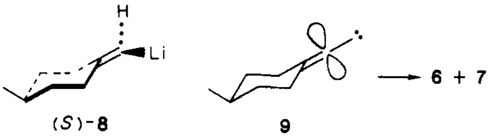


6



7

There are surprising results. First is the observation that **3** was obtained with 100% optical purity and complete *retention rather than inversion of configuration.* Previously it was found that (S-(+)-**1** (X = Cl), in ether at −75 °C, yielded (R-(−)-**3**, 31% optically pure[8] and of *inverted configuration.* Second is the formation of **6** and **7** which are products that were not observed in the reaction of (S)-(+)-**1** (X = Cl) with *tert*-butyllithium. However, both **6** and **7** (1:1) were obtained in the reaction of (S)-(+)-**1** (X = Br) because, besides metalation of the bromide to yield carbenoid, halogen metal exchange also occurred to produce the stable vinyllithium **8**.[7,9] This latter reaction does not occur when X = Cl. The α-addition of **8** to the carbene **9**, formed from carbenoid, gave a 1:1 mixture of adduct[3] which upon hydrolysis yielded **6** and **7**. Based on the previously established[10] absolute configuration and optical purity, **6** was formed with 50% optical purity[11] and overall *retention of configuration.*



To account for these observations we postulate that the highly electronegative fluorine is playing a role by coordinating with another molecule *tert*-butyllithium and thereby directing the *tert*-butyl group to enter by what could be considered an S_Ni mechanism (Scheme II, path a) which leads to a stereospecific retention of configuration. As positive charge develops, the vinyl carbocation intermediate (carbenoid) becomes more of a loose ion pair and it can then become a good hydride abstractor and remove hydride from the *tert*-butyl group to produce (S)-**8** and isobutylene[12] (Scheme II, path b). In this loose ion pair some chirality can be lost and the partially racemized (S)-**8** can then add to the carbene product **9** to yield **6** and **7** in an expected 1:1 ratio.[11]

If this postulate is correct then the use of perdeuterio-*tert*-butyllithium should give rise to (R)-(−)-**3** possessing a perdeuterio-*tert*-butyl group and to (S)-**8** containing a 1-deuterio atom which then condenses with carbene to yield **6** and **7** each possessing one vinyl deuterium atom. This is precisely what is observed.[3,13]

Fluorine not only participates in metal-assisted ionization by strong lithium coordination but also plays a unique role in directing the incoming nucleophile, *tert*-butyl or hydride.

Supplementary Material Available: Crystal data and tables of interatomic distances, selected bond angles, selected torsional angles, and positional and thermal parameters and their estimated standard deviations for $C_{19}H_{26}FNO_2$ (6 pages); table of structure factors F_{obsd} and F_{calcd} for $C_{19}H_{26}FNO_2$ (6 pages). Ordering information is given on any current masthead page.

---

(8) At this time it is not known whether the difference in optical purity is due to a difference in temperature, −100 °C vs. 75 °C.

(9) Vinyllithium (7) does not form (S)-1 (X = Cl) since chlorides do not undergo halogen metal exchange at an appreciable rate.

(10) Walborsky, H. M.; Banks, R. B.; Banks, M. L. A.; Duraisamy, M. *Organometallics* **1982**, *1*, 667. (b) Banks, R. B.; Walborsky, H. M. *J. Am. Chem. Soc.* **1976**, *98*, 3732.

(11) This takes into account that the mixture contains 50% of inactive *meso*-7. Since 6 was found to be 50% optically pure it implies that 8 consisted of 75% S and 25% R configurations. Addition of this mixture of enantiomers to an achiral carbene 9 would lead to a 1:1 mixture of 6 and 7 with 6 being 50% optically pure.

(12) For other examples of hydride abstractions by carbenoid intermediates, see: Ritter, R. H.; Cohen, T. *J. Am. Chem. Soc.* **1986**, *108*, 3718. Harada, T.; Maeda, H.; Oku, A., *Tetrahedron Lett.* **1985**, *26*, 6489.

(13) All new compound gave satisfactory elemental analyses. Deuterium content was determined by NMR and mass spectral analyses.

Reaction of Ethylene with a Coordinatively Unsaturated Iron Complex, Fe(DEPE)$_2$: sp^2 C–H Bond Activation without Prior Formation of a π-Complex

Murray V. Baker and Leslie D. Field*

Department of Organic Chemistry, University of Sydney
Sydney, N.S.W. Australia 2006

Received July 17, 1986

In the reaction of coordinatively unsaturated transition metals with alkenes and arenes, the formation of a π-complex prior to sp^2 C–H activation has frequently been invoked to account for the relative ease of C–H activation. In a study of the reaction of the iridium complex $(\eta^5\text{-Me}_5C_5)IrPMe_3$, however, it has been demonstrated that insertion of the iridium center into the sp^2 C–H bonds of ethylene proceeds with concurrent and not prior formation of a π-complex.[1] We recently reported[2] that the coordinatively unsaturated iron complex Fe(DMPE)$_2$ (**1a**)[3] [DMPE = 1,2-bis-

---

(1) Stoutland, P. O.; Bergman, R. G. *J. Am. Chem. Soc.* **1985**, *107*, 4581-4582.

(2) Baker, M. V.; Field, L. D. *J. Am. Chem. Soc.*, in press.

(3) For earlier studies on the chemistry of Fe(DMPE)$_2$, see: (a) Tolman, C. A.; Ittel, S. D.: English, A. D.; Jesson, J. P. *J. Am. Chem. Soc.* **1978**, *100*, 4080-4089. (b) Tolman, C. A.; Ittel, S. D.; English, A. D.; Jesson, J. P. *J. Am. Chem. Soc.* **1978**, *100*, 7577-7585. (c) Tolman, C. A.; Ittel, S. D.; English, A. D.; Jesson, J. P. *J. Am. Chem. Soc.* **1979**, *101*, 1742-1751. (d) Bergamini, P.; Sostero, S.; Traverso, O. *J. Organomet. Chem.* **1986**, *299*, C11-C14.

0002-7863/86/1508-7436$01.50/0