Table I
Products from Metalation of 1 and Reaction with Benzaldehyde under Various Conditions[a]

Metalation temp, °C	Mode of addition	Time, hr	Yield, %	Products	
				3	**4**
−80	Inverse	1	28	1.00	
−15	Inverse	1	60	1.00	
0	Inverse	1	82	1.00	
−15	Normal	1	62	0.75	0.25
−15	Normal	1	~70	0.75	0.25

[a] Reactions run in ether.

dehyde leads to **5**; no evidence for the product analogous to **4** ($R_1 = CH_3$) was obtained.

Variation of the position of metalation with conditions has previously been observed with 2-methylthiazole (**7**). Crousier and Metzger[4] reported a careful study of the metalation of **7**, with low temperature favoring metalation at the methyl group rather than in the ring, and we have confirmed these results.[5] More recently Meyers and Knaus[6] have reported the results of additional studies of the metalation of 2-methylthiazoles, and have indicated that the nature of the products which may be obtained is often complex.

Thus the present results show an additional instance of alternate modes of reaction, annular *vs.* lateral metalation of methyl-substituted azoles.

Experimental Section[7]

1-Phenyl-2-(1-methyl-2-imidazolyl)ethanol (3). To a cooled solution of 4.8 g (0.05 mol) of **1**[8] in 250 ml of anhydrous ether was added 35 ml (0.056 mol) of butyllithium in hexane. The reaction mixture was maintained at 0° under nitrogen for 1 hr, and then 10.6 g (0.1 mol) of benzaldehyde was added. After 30 min the reaction mixture was quenched by the addition of 300 ml of 2 *N* HCl. The phases were separated and the aqueous phase was made alkaline with potassium carbonate. The precipitated solid was removed by filtration, and recrystallized from benzene–hexane. 1-Phenyl-2-(1-methyl-2-imidazolyl)ethanol, 8.3 g (82%), was obtained: mp 137–138.5°; nmr ($CDCl_3$) δ 7.28 (s, 5, phenyl), 6.88 (d, 1, $J = 6.4$ Hz, CH_2CHOH), 3.38 (s, 3, NCH_3), and 2.92 (d, 2, $J = 6.4$ Hz, CH_2CHOH).

Anal. Calcd for $C_{12}H_{14}N_2O$: C, 71.26; H, 6.98; N, 13.85. Found: C, 71.41; H, 7.04; N, 13.62.

1-Phenyl-2-(1-methyl-2-imidazolyl)ethanol (3) and 1,2-Dimethyl-α-phenylimidazole-5-methanol (4). Metalation was carried out by the slow addition of 1,2-dimethylimidazole to butyllithium in hexane at −15° following the procedure of Tertov, *et al.*[2] To the formed lithio derivative, benzaldehyde was added. Isolation in the usual fashion led to a crude solid, mp 134–138°, in 63% yield, which by nmr spectrum was 75% **3** and 25% **4**. A recrystallization from benzene–hexane led to the formation of two distinct crystalline forms, small clustered rosettes and chunky crystals. These were separated by hand. The rosettes showed mp 178–179° (reported[2] mp 177–178°) and an nmr spectrum in accord with the structure for compound **4**. The chunky crystals were the major component, compound **3**, mp 136–138° and nmr as reported above. Further confirmation for the two different structures was additionally obtained from the mass spectra. Compound **4** shows a unique *m/e* 144 peak; compound **3** shows a strong *m/e* 184 (M − 18) peak.

1-(1-Methyl-2-imidazolyl)-2-propanol (5). To a solution of 9.6 g (0.1 mol) of **1** in 500 ml of dry ether at 0° under nitrogen was added 70 ml (0.11 mol) of butyllithium (1.6 *M* in hexane, Foote Mineral Co.). After stirring for an additional 0.5 hr, 200 ml of 2 *N* HCl was added. The separated ether–hexane phase was washed with HCl, and the combined aqueous solutions were made alkaline with potassium carbonate and extracted with $CHCl_3$. The dried (Na_2SO_4) chloroform extracts were concentrated under reduced pressure to afford an orange oil. The crude mixture was chromatographed on silica gel eluting with $CHCl_3$ to afford 3.25 g of recovered dimethylimidazole (34%), and then with $CHCl_3$-5% methanol to afford 5.3 g (38%) of **5**: mp 71–72°; nmr ($CDCl_3$) δ 6.71 (m, 2, C_4 H, C_5 H), 4.15 [m, 1, $CH_2CH(OH)CH_3$], 3.50 (s, 3, NCH_3), 2.65 (d, 2, $J = 6.2$ Hz, CH_2CHOH), and 1.22 [d, 3, $J = 6.2$ Hz, $CH(OH)CH_3$].

Anal. Calcd for $C_7H_{12}N_2O$: C, 59.98; H, 8.63; N, 19.98. Found: C, 59.71; H, 8.44; N, 19.84.

Addition of 1,2-dimethylimidazole (1.6 g in 10 ml of ether) to a cooled (−15°) solution of butyllithium in hexane, followed by addition of acetaldehyde, gave a 50% yield of **5**, with no evidence for the isomer, 1-(1,2-dimethyl-5-imidazolyl)ethanol, evidenced in the nmr of the crude reaction product.

1-(1-Methyl-2-imidazolyl)-2-phenyl-2-propanol (6). Metalation of 1,2-dimethylimidazole was carried out by the addition of butyllithium to 1,2-dimethylimidazole in ether at −15°. Addition of acetophenone and work-up in the usual manner afforded a crude solid, which was crystallized from benzene–hexane to afford **6**, mp 151–153°, in 60% yield with an nmr spectrum appropriate for the assigned structure.

Anal. Calcd for $C_{13}H_{16}N_2O$: C, 72.19; H, 7.46; N, 12.95. Found: C, 72.25; H, 7.26; N, 12.82.

Registry No.—**1**, 1739-84-0; **3**, 51593-79-4; **4**, 24134-10-9; **5**, 51593-80-7; **6**, 51593-81-8; butyllithium, 109-72-8; benzaldehyde, 100-52-7; acetaldehyde, 75-07-0; acetophenone, 98-86-2.

References and Notes

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(7) Melting points are uncorrected. Nmr spectra were obtained using a Varian Associates Model T-60 spectrometer and internal TMS. Elemental analyses were determined by the Chemical Analytical Services Laboratory, College of Chemistry, University of California, Berkeley, Calif.
(8) Prepared by the method of M. Haring, *Helv. Chim. Acta*, **42**, 1845 (1959). 1,2-Dimethylimidazole slowly crystallized to a low-melting solid, mp ~30°.

A Mixture of Mechanisms in the Reaction of Tosylhydrazones with Alkyllithium Reagents

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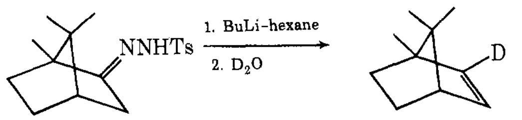
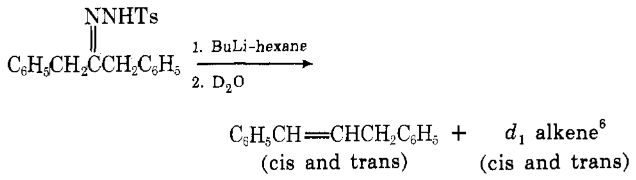
Several years ago we reported that camphor tosylhydrazone reacts with methyllithium in ether to give 2-bornene.[1,2] It was noted that when the reaction mixture was quenched with D_2O only minor amounts of deuterium were incorporated into the alkene. Careful examination of the reaction mixture revealed that ethanol was present after quenching. Other tosylhydrazone decompositions followed by D_2O quenching led to up to 60% incorporation of deuterium, but in no experiment was complete deuteration effected. These results led to the conclusion that if a vinyl anion was a reaction intermediate, it appeared to react partially, even mostly in some cases, with solvent before the reaction mixture was quenched.[1]

Potentially the reaction of tosylhydrazones with alkyllithium reagents could be a useful method of introducing vinyl deuterium, or other electrophiles, into alkenes, but the reaction with solvent apparently destroys the intermediate and thereby inhibits its usefulness.

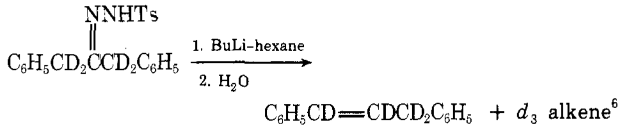
We have now succeeded in incorporating deuterium into 2-bornene by employing the non-proton-donating solvent hexane, but have also discovered that a third mechanism of vinyl anion neutralization, along with reaction with solvent and quenching with water, may occur. Camphor tosylhydrazone reacts with *n*-butyllithium in hexane[3] and when the reaction is quenched with D_2O, 2-bornene-*2*-d_1 containing 95% deuterium (mass spectrometry) is obtained. The yield of alkene is inferior to that obtained in ether, probably because of the insolubility of the tosylhydrazone in hexane.



Attempts to incorporate deuterium into several other alkenes employing this technique, however, were far less successful. For example, the cis and trans isomers of 1,3-diphenylpropene generated from 1,3-diphenyl-2-propanone tosylhydrazone[4] after D_2O quenching give a mixture of labeled and unlabeled alkene.[5] Moreover, 1,3-diphenyl-2-propanone-*1,1,3,3*-d_4 tosylhydrazone gives a mixture of d_3 and d_4 alkenes.

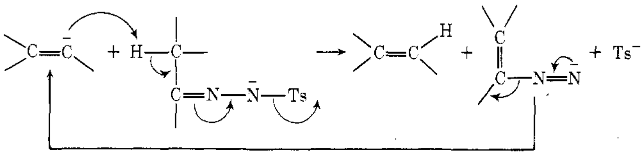


$$C_6H_5CH_2\overset{\overset{\text{NNHTs}}{\|}}{C}CH_2C_6H_5 \xrightarrow[\text{2. } D_2O]{\text{1. BuLi-hexane}} \underset{\text{(cis and trans)}}{C_6H_5CH{=}CHCH_2C_6H_5} + \underset{\text{(cis and trans)}}{d_1 \text{ alkene}^6}$$



$$C_6H_5CD_2\overset{\overset{\text{NNHTs}}{\|}}{C}CD_2C_6H_5 \xrightarrow[\text{2. } H_2O]{\text{1. BuLi-hexane}} C_6H_5CD{=}CDCD_2C_6H_5 + d_3 \text{ alkene}^6$$

A carbene mechanism would give the d_4 alkene, but must be precluded by the high cis to trans ratio of the product.[4] It is therefore proposed that the third mechanism of vinyl anion neutralization involves proton abstraction from the α position of a tosylhydrazone salt in a chain reaction.



The reaction of 1,3-diphenyl-2-propanone tosylhydrazone, and similar acyclic systems, with alkyllithium reagents is further complicated by the fact that the geometric isomer ratio is affected by solvent changes and by reaction times. Investigations of the factors affecting these reactions are in progress at present. In light of the results with acyclic systems, it appears that the vinyl anion generated from camphor tosylhydrazone is reluctant to attack the tosylhydrazone salt, presumably for steric reasons.

Experimental Section

2-Bornene-*2*-d_1. To a suspension of camphor tosylhydrazone[7] (3.2 g, 0.01 mol) in 50 ml of dry hexane was added 15 ml of *n*-butyllithium in hexane (2.0 *M*, 1.92 g, 0.03 mol) over 30 min. The suspension, which turns orange-yellow, was allowed to stir for 16 hr at room temperature and excess D_2O was carefully added. Water and ether were added and the layers were separated. The 2-bornene was isolated as previously described[2] and the yield was 643 mg (47%), mp 105-110°. A low-voltage mass spectrum (15 eV) showed the 2-bornene to be 95% d_1 and 5% d_0. The position of the deuterium was determined by pmr. Unlabeled 2-bornene shows a one-proton doublet at 5.62 ppm (J = 6 Hz) and a one-proton multiplet at 5.85 ppm. The labeled 2-bornene obtained in this experiment shows a one-proton broadened doublet centered at 5.85 ppm. 2-Bornene-*3*-d_1[1] obtained from camphor-*3,3*-d_2 tosylhydrazone[8] and methyllithium shows a one-proton broadened singlet at 5.60 ppm.

Registry No.—Camphor tosylhydrazone, 10224-32-5; *n*-butyllithium, 109-72-8; 2-bornene-*2*-d_1, 51472-55-0.

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Molybdenum Hexacarbonyl Catalyzed Acylation of Ferrocene

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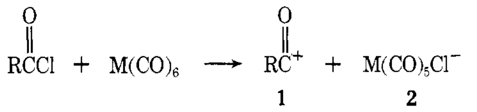
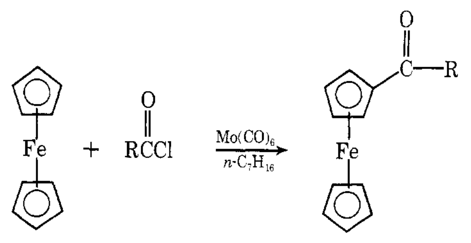
One of us recently showed that group VI metal carbonyls, particularly molybdenum hexacarbonyl [$Mo(CO)_6$], are useful catalysts for the reaction of ethers and acid halides.[1] The reaction was proposed to occur *via* initial formation of an acylium ion (**1**) and a metal pentacarbonyl halide anion (**2**). If such a process indeed occurs, then it



$$R\overset{\overset{O}{\|}}{C}Cl + M(CO)_6 \longrightarrow \underset{\mathbf{1}}{R\overset{\overset{O}{\|}}{C}{}^+} + \underset{\mathbf{2}}{M(CO)_5Cl^-}$$

should be possible to acylate metallocenes such as ferrocene. We now wish to report that Friedel–Crafts acylation of ferrocene, and presumably other metallocenes, can be effectively catalyzed by $Mo(CO)_6$.

Treatment of a series of acid chlorides with ferrocene in *n*-heptane, and using a catalytic quantity of $Mo(CO)_6$, gave reasonable to very good yields of acylated ferrocenes (**3**).



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The yields and melting points of the products are listed in Table I. In several instances (*e.g.*, **3**, R = 1-adamantyl)[2] the yields obtained are superior to those reported

Table I
Yields and Melting Points of Acylated Ferrocenes

3, R =	Yield,[a] %	Mp, °C	Lit. mp, °C
CH_3	76	84.0–85.0	85.0–86.0[b]
$(CH_3)_2CH$	41	Oil	Oil[c]
Cyclohexyl	50	76.0–78.0	79[d]
1-Adamantyl	76	144.5–145.5	147.0–148.0[e]
C_6H_5	73	109.0–110.0	108.1–108.3[b]

[a] Yields are of pure **3** and are based on unrecovered ferrocene. [b] R. C. Weast, Ed., "Handbook of Chemistry and Physics," 50th ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1969. [c] R. J. Stephenson, British Patent 864,197 (1961); *Chem. Abstr.*, **55**, 17647 (1961). [d] T. Leigh, British Patent 819,108 (1959); *Chem. Abstr.*, **54**, 7732*d* (1960). [e] Reference 2.