Hz, 2 H), 7.52 (center of AB system, J = 16 Hz, 2 H), and 8.6 (br s, 2 H).

Analysis of the distilled mixture gave the following results.

Anal. Calcd for $C_{11}H_{11}Br$: C, 59.2; H, 4.93. Found: C, 59.6; H, 5.09.

Reduction of 7,7-Dibromobicyclo[4.1.0]heptane (4). In a manner analogous to the above, 15 g of zinc–copper couple, 10 g (0.04 mol) of **4**, and 5 ml of deuterium oxide in 200 ml of dry ether were stirred at room temperature for 24 hr. The solution was filtered through Celite, and the filtrate was worked up as usual. After distillation of the ether, the residue was vacuum fractionated to yield 0.70 g (18.5%) of **5**, bp 67–68° (110 mm) [lit.[17] bp 110° (760 mm)], and 4.20 g (62%), bp 83–86° (10 mm) [lit.[3] bp 96–99° (36 mm)], of an endo–exo mixture of **6a** and **6b**. Vpc analysis showed an endo/exo ratio of 8.2.

Reduction of 7,7-Dichlorobicyclo[3.2.0]hept-2-en-6-one (8). To 20 g of zinc–copper couple as prepared above in 80 ml of anhydrous tetrahydrofuran was added 4 g (0.023 mol) of **8** and 5 ml of deuterium oxide. The reaction mixture was stirred at 65° for 6 hr, filtered through Celite, and then diluted with 300 ml of water. The aqueous phase was extracted with pentane (6 × 75 ml) and the combined pentane extracts were worked up in the usual manner. Vacuum distillation yielded 1.8 g (72%) of **10**, bp 69–70° (30 mm) [lit.[14a] bp 62° (20 mm)]. Vpc analysis indicated >99% purity and nmr integration indicated a minimum of 95% dideuteration.

Reduction of 8,8-Dichlorobicyclo[4.2.0]oct-2-en-7-one (7). In a procedure analogous to the above, 12 g of zinc–copper couple, 95 ml of tetrahydrofuran, 2.07 g (0.01 mol) of **7**, and 5 ml of deuterium oxide were heated for 6 hr at 70°. Work-up as above followed by molecular distillation afforded 1.07 g (80%) of **9**, bp 64–65° (15 mm) [lit.[14a] bp 69–78° (5 mm)], homogeneous by vpc.

Reduction of 3-Chloro-5,5-dimethylcyclohex-2-enone (11). To a magnetically stirred solution of 4 g (0.025 mol) of **11** in 75 ml of tetrahydrofuran and 50 ml of ethyl ether was added 8 g of zinc-copper couple. The reaction mixture was stirred at room temperature for 6 hr and then filtered through Celite. The filtrate was poured into 200 ml of water followed by extraction with ether (4 × 100 ml). The combined ether layers were then worked up as usual. After distillation of the solvent, vacuum distillation yielded 2.2 g (75%) of 5,5-dimethylcyclohex-2-enone (**12**), bp 96–98° (34 mm) [lit.[18] bp 88° (32 mm)].

Preparation of 7,7-Dibromo-3,4-benzobicyclo[4.1.0]heptane (1). To a stirred mixture of 25.4 g (0.27 mol) of freshly prepared potassium *tert*-butoxide and 57 g (0.44 mol) of 1,4-dihydronaphthalene at 5–10° was added 58 g (0.23 mol) of bromoform dropwise over a period of 1 hr. The reaction mixture was then stirred at room temperature for 0.5 hr, 200 ml of water was added, and the solution was extracted with ether (3 × 100 ml). The combined ether extract was washed in 5% hydrochloric acid (100 ml) and then worked up as usual, yielding a red oil. The unreacted 1,4-dihydronaphthalene was distilled off and the product was collected as a yellow oil which solidified on standing, bp 104–110° (20 mm). Crystallization of this material from hexane yielded in several crops 36 g (52%) of **1** as a white, crystalline solid: mp 65–67°; ir (KBr) 6.58 (m), 6.89 (w), 7.02 (m), 7.69 (w), 9.63 (m), 10.52 (w), 11.02 (m), 13.28 (s), and 14.04 μ (s); nmr (CCl_4) τ 3.0 (s, 4 H), A_2B_2 centered at 7.1 with lower field component showing addition coupling (4 H), and 7.96 (m, 2 H).

Anal. Calcd for $C_{11}H_{10}Br_2$: C, 43.7; H, 3.31. Found: C, 43.9; H, 3.4.

Registry No.—1, 40467-32-1; **3a,** 51593-45-4; **3b,** 51703-88-9; **4,** 2415-79-4; **5,** 51592-70-2; **6a,** 51593-46-5; **6b,** 51593-47-6; **7,** 51592-71-3; **8,** 5307-99-3; **9,** 51592-72-4; **10,** 51592-73-5; **11,** 17530-69-7; **12,** 4694-17-1; 1,4-dihydronaphthalene, 612-17-9; bromoform, 75-25-2.

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Alternate Positions of Metalation of 1,2-Dimethylimidazole with Butyllithium

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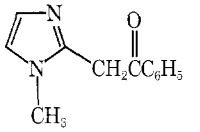
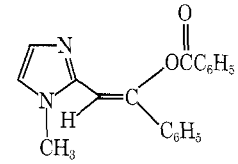
In conjunction with our studies of the preparation and solvolysis of imidazolylethanol derivatives,[1] the report by Tertov, Burykin, and Sadekov[2] that 1,2-dimethylimidazole (**1**) was metalated in the 5 position drew our interest. In our hands the course of the reaction is substantially different and more complex than indicated by the Russian authors. A recent report[3] of the reaction of 1,2-dimethylimidazole with benzoyl chloride to give rise to lateral substitution products (**2a**, **2b**) prompts a report of our results at this time.

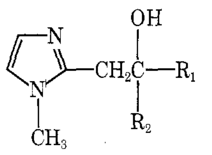


2a



2b

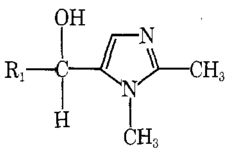
At −80°, metalation of **1** proceeds slowly. The lithio derivative which is formed by addition of butyllithium to 1,2-dimethylimidazole reacts with benzaldehyde to give 1-phenyl-2-(1-methyl-2-imidazolyl)ethanol (**3**) in 28% yield, and not 1,2-dimethyl-α-phenylimidazole-5-methanol (**4**). Improved yields of **3** result at higher temperatures. When metalation is carried out in a normal fashion (addition of **1** to butyllithium at −15°) a mixture of **3** and **4** results, but in our hands the predominant product is **3**, not **4**, as reported by Tertov, *et al.*[2]



3, $R_1 = C_6H_5$; $R_2 = H$

5, $R_1 = CH_3$; $R_2 = H$

6, $R_1 = C_6H_5$; $R_2 = CH_3$



4, $R_1 = C_6H_5$

Results obtained under other experimental conditions are summarized in Table I.

We also prepared **5** and **6**. Using both normal and inverse conditions for the metalation of **1**, reaction of acetal-

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	Products 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.

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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