Cyclohexyl Metal Compounds. III. Stereochemistry of Some Substitution Reactions at the Carbon–Lithium Bond

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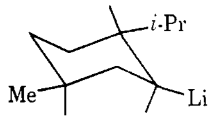
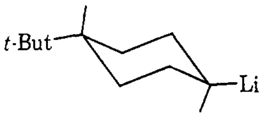
Several reactions of menthyl- and 4-*t*-butylcyclohexyllithium which result in substitution at the carbon–metal center have been studied. Configurations of products (axial/equatorial ratios) indicate that most common substitution reactions such as carbonation, protonolysis, and coupling proceed with predominant retention of configuration. A four-center S_Ei transition state is postulated for some reactions, although a six-center mechanism involving the dimer of the lithium reagent represents a reasonable alternative in other cases. Halogenations with Cl_2, Br_2, and I_2 result in significant, and often predominant, inversion of configuration. A backside S_E2 attack at the carbon atom, perhaps involving halogen radicals, is postulated. Bromination with 1,2-dibromoethane, bromobenzene, and pyridine–bromine complex results in predominant retention of configuration, and apparently proceeds *via* a concerted, multicenter process.

Previous papers in this series have described the preparation of two cyclohexyllithium derivatives, (+)-menthyllithium[1] (I) and 4-*t*-butylcyclohexyllithium[2] (II), which apparently are configurationally stable in hydrocarbon solvents for indefinite periods of time. In the case of menthyllithium, configurational stability was indicated by an analysis of the proton nmr spectrum and confirmed by carbonation products. In fact, the use of carbonation to establish the configuration of lithium and magnesium organics has only recently been verified,[3,4] and the aforementioned results with menthyllithium represent an independent verification of the carbonation method. Although similar nmr evidence was not conclusive for 4-*t*-butylcyclohexyllithium due to solubility limitation, carbonation yielded only a single acid, *trans*-4-*t*-butylcyclohexylcarboxylic acid, from which the structure of the lithium compound was inferred.



I



II

As pointed out earlier,[1] we interpret the available evidence to indicate that cyclohexyllithium compounds, indeed all aliphatic organolithiums, are not to be characterized as ionic (dissociated) compounds. Although it is clear that the carbon–metal bond should be quite polar, the molecule is able to delocalize this charge effectively by the formation of multicenter, so-called electron-deficient bonds for which alkyllithiums are well known.[5] It is only when the organic portion of the molecule is able to delocalize the charge effectively, *e.g.*, in benzyl-, fluorenyl-, and triphenylmethyllithium, that ionic properties are evident. Of course, the absence of ionic species in the ground state of alkyllithiums would not necessarily preclude the participation of ionic intermediates in the reactions of these compounds. In fact, many chemists have assumed that alkyllithiums act as carbanion sources, and many textbooks continue to represent their reactions as processes which involve transient carbanions. If a solvent-separated carbanion–cation pair $R^-||Li^+$ is the active intermediate in the reactions of cycloalkyllithium compounds, we would expect that some loss of stereospecificity would occur. Carbanions, being isoelectronic with amines, presumably would have rather low barriers to inversion (8–14 kcal/mol),[7] and a mixture of epimeric products would be expected from the reactions of cycloalkyllithiums with various electrophilic substitution reagents (eq 1–3; R_e and R_a represent cyclohexyl radicals with equatorial- and axial-substituted heteroatoms, respectively).[8-10]

$$R_eLi \rightleftarrows R_e^-||Li^+ \rightleftarrows R_a^-||Li^+ \rightleftarrows R_aLi \qquad (1)$$

$$R_e^-||Li^+ + EN \longrightarrow R_eE + LiN \qquad (2)$$

$$R_a^-||Li^+ + EN \longrightarrow R_aE + LiN \qquad (3)$$

Some information concerning the stereochemistry of substitutions at the carbon–lithium bond is available from the works of Walborsky[10] and Applequist.[11,12] With the exception of reactions with molecular halogens,[13] all of the reactions studied appear to involve predominant retention of configuration.

The present paper describes the products obtained from the reaction of menthyllithium and *trans*-4-*t*-butylcyclohexyllithium with a variety of reagents including the halogens, and provides further evidence relating to the mechanism of these reactions.

Results and Discussion

Menthyl- and *trans*-4-*t*-butylcyclohexyllithium react with a variety of substrates to yield substitution

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[1] W. H. Glaze and C. M. Selman, *J. Org. Chem.*, **33**, 1987 (1968).

[2] W. H. Glaze and C. M. Selman, *J. Organometal. Chem.*, **11**, P3 (1968).

[3] D. Seyferth and L. G. Vaughan, *ibid.*, **1**, 201 (1963).

[4] F. R. Jensen and K. L. Nakamaye, *J. Amer. Chem. Soc.*, **88**, 3437 (1966).

[5] We shall soon reveal the results of LCAO-MO-CNDO calculations[6] for methyllithium monomer, dimer, and tetramer which illustrate the delocalization of charge at the lithium and α-carbon atoms due to oligomer formation.

[6] J. A. Pople and G. A. Segal, *J. Chem. Phys.*, **44**, 3298 (1966).

[7] G. W. Koeppl, D. S. Sagatys, G. S. Krishnamurthy, and S. I. Miller, *J. Amer. Chem. Soc.*, **89**, 3396 (1967).

[8] Waack and coworkers[9] have recently observed that ^{7}Li exchange between LiBr and CH_3Li in ether is very rapid at room temperature, and have concluded on the basis of Walborsky's earlier work[10] that the exchange process occurs with retention of configuration. It should be noted, however, that the exchange process measured by Waack is probably induced by the formation of a LiBr–CH_3Li complex, and for that reason the observation of rapid ^{7}Li exchange does not provide any information concerning the participation of carbanions in the reactions of alkyllithiums.

[9] R. Waack, M. A. Doran, and E. B. Baker, *Chem. Commun.*, 1291 (1967).

[10] H. M. Walborsky, F. J. Impastato, and A. E. Young, *J. Amer. Chem. Soc.*, **86**, 3283, 3288 (1964).

[11] D. E. Applequist and A. G. Peterson, *ibid.*, **83**, 862 (1962).

[12] D. E. Applequist and G. W. Chmurny, *ibid.*, **89**, 875 (1967).

[13] Bromination of 2,2-diphenyl-1-methylcyclopropyllithium[10] reportedly proceeds with exclusive retention of configuration in contrast to the less specific bromination of *cis*-2-methylcyclopropyllithium[11] and 2-norbornyllithium.[12]

products with predominant retention of configuration. These reactions include carbonation (97% retention) and protonolysis (95% retention) which we have previously reported.[1,2] Protonolysis was studied by reaction of the cyclohexyllithium compounds in pentane solvent with deuterium oxide and several deuterated alcohols (eq 4, R = D, CH_3, C_2H_5, i-C_3H_7, t-C_4H_9). As

$$R'Li + DOR \longrightarrow R'D + LiOR \qquad (4)$$

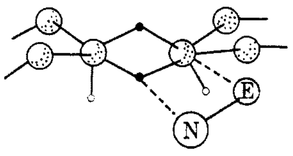
described in the Experimental Section, the configuration of the hydrocarbon product was determined by analysis of the C–D stretching region of the infrared spectrum. These reactions are quite rapid and result in high yields of substitution product.

Reactions with methyl iodide or bromobenzene are not so specific, however, and a mixture of products results in each case. The predominant reaction (*ca.* 60% yield) is halogen–lithium interconversion which results in the precipitation of methyl- or phenyllithium from hydrocarbon solution (eq 5). The configuration of the

$$RLi + R'X \longrightarrow RX + R'Li\downarrow \qquad (5)$$

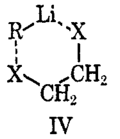
alkyl halide RX was determined by nmr[1,2] and glpc. Predominant retention of configuration was observed for both reactions (90 and 85% retention for CH_3I and C_6H_5Br, respectively).

These results may be rationalized in terms of an SEi four-center transition state, as shown in III.[14] Such transition states are commonly used to describe carbonation[4] and halogen–metal exchange[10] reactions, which have generally been assumed to occur with predominant retention of configuration. The results are not consistent with our expectations of carbanion behavior as discussed in the introductory section of this paper. However, a mechanism involving induced dissociation into *contact* ion pairs in which a directional bond is retained may not be excluded by the available evidence.



III, •, lithium; ○, hydrogen; ◌, carbon

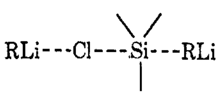
Bromination of I and II with 1,2-dibromoethane also yields predominant retention of configuration (97%). A six-membered transition state IV has been discussed for this reaction.[12] An alternative, but not necessarily preferable, explanation is that simple halogen–metal exchange (eq 6) yields 2-bromoethyllithium which is presumably unstable at the temperature used.



IV

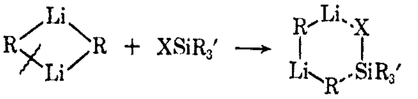
$$\begin{array}{l} RLi + BrCH_2CH_2Br \longrightarrow RBr + LiCH_2CH_2Br \\ \hspace{8em}\downarrow \\ \hspace{6em} LiBr + C_2H_4 \qquad (6) \end{array}$$

The coupling of I and II with chlorotrimethylsilane in pentane or 2:1 pentane–ether solution also yields products with predominant retention of configuration (90–95% retention).[16,17] The results provide an interesting comparison with the results obtained by Sommer and coworkers,[18,19] who studied the reactions of various alkyllithiums with optically active α-naphthylphenylmethylsilyl halides, hydrides, and methoxides. Although the stereochemistry at silicon depends on the nature of the alkyllithium and the substituent at silicon, *inversion* was observed in every case with the silyl chlorides. Transition state IV was proposed for the inversion process, although no documentation for the trimolecular nature of IV was offered. The present results indicate that backside attack on the carbon of the lithium reagent by the silicon atom should not be inferred from IV. On the basis of the very limited information which is now available, we prefer to consider the reaction with silyl chlorides to proceed *via* a transition state V quite similar to that proposed by Sommer to account for retention reactions with silyl fluorides. Such a configuration could easily form by the breaking of one lithium–carbon bridge bond in the dimer, and may account for both retention and inversion processes in silylation reactions. In the case of X = F, H, and OMe where Si–X bond lengths are either short or where π bonding to X is most prevalent, and where Li–X bond distances in V are expected to be short, the X–Si–R angle in V should be minimized. It is only when this angle increases, approaching 180°, that inversion is expected. In the case of the silyl chloride, transition state V will be more open, and the X–Si–R angle will be greater, thus allowing inversion at the silicon atom to occur. In both of these processes, configuration at the carbon atom of the lithium reagent is maintained. An alternate way to express the argument given above is to say that close approach of X to the Li atom necessitates the entering group R to assume one of the equatorial rather than apical positions in the silicon pentacovalent



$$RLi\text{---}Cl\text{---}Si\text{---}RLi$$

IV



V

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(14) The alkyllithium in III is drawn in dimeric form to illustrate possible steric factors that may arise when an oligomeric alkyllithium is the kinetically active species. Although no conclusive data are presently available regarding the degree of association of the active intermediate in hydrocarbon solvents, the ^{7}Li exchange data obtained by Brown[15] suggest that the dimer is responsible for intermolecular exchange. The dissociation of the oligomer into monomer units is apparently endothermic by approximately 35 kcal/mol,[1,15] compared to approximately 18 kcal/mol for dissociation into dimers. Although monomeric units may be formed by strongly polar substrates, or solvents, the concept of reactive dimers will be utilized in our discussion until further information is available.

(15) T. L. Brown, *J. Organometal. Chem.*, **5**, 188 (1966).

(16) Although the reaction of alkyllithiums with chlorotrimethylsilane is accelerated by the addition of ether, the distribution of products (*e.g.*, menthyl- and neomenthyltrimethylsilane) is uneffected. A single-electron-transfer mechanism[17] may predominate in the presence of ether, however, in which case the present results point to retention of configuration in whatever process results in carbon–silicon bond formation.

(17) C. G. Screttas and J. F. Eastham, *J. Amer. Chem. Soc.*, **88**, 5668 (1966).

(18) L. H. Sommer and W. D. Korte, *ibid.*, **89**, 5802 (1967).

(19) L. H. Sommer, W. D. Korte, and P. G. Rodewalk, *ibid.*, **89**, 862 (1967).

coordination sphere,[18,19] thus resulting in retention of configuration at the silicon atom. These comments are to be taken as preliminary at this stage, and a more thorough kinetic and mechanistic study of the reaction of silyl derivatives and lithium reagents is now in progress.

In Table I are listed the isomer distributions obtained from halogenations of menthyl- and 4-*t*-butylcyclohexyllithium. It is apparent that retention of configuration is not the rule in the case of reactions with molecular halogens. This result is consistent with the results of Applequist and Chmurny who found considerable inversion upon bromination with Br_2 of 2-norbornyllithium.[12] Although a dual mechanism cannot be eliminated at this time, we prefer to rationalize the results in Table I in terms of direct attack by the halogen at the carbon of the lithium reagent, without rupture of the RLi oligomer. Molecular models of the tetramer and dimer of cyclohexyllithiums suggest that backside attack should be more favorable for steric reasons if the oligomer is not destroyed. The results also may be interpreted in terms of attack by halogen atoms which may be formed, for example, by a single-electron-transfer process[17] as shown in eq 7–9. However, it is doubtful that free

$$(\mathrm{RLi})_n + \mathrm{X}_2 \longrightarrow (\mathrm{RLi})_n\cdot^{+} + \mathrm{X}_2\cdot^{-} \tag{7}$$

$$\mathrm{X}_2\cdot^{-} \longrightarrow \mathrm{X}\cdot + \mathrm{X}^{-} \tag{8}$$

$$\mathrm{X}\cdot + (\mathrm{RLi})_n\cdot^{+} \longrightarrow \mathrm{RX} + \mathrm{Li}^{+} + (\mathrm{RLi})_{n-1} \tag{9}$$

alkyl radicals are formed in view of the high degree of inversion observed in many of the halogenation reactions and the variations observed between the halogens.[11,20] Reactions with bromine dissolved in pyridine, which yields predominant retention of configuration, apparently proceed by a multicenter transition state such as III or V. Pyridine–bromine complex is apparently more polar than free Br_2 and may be capable of rupturing the alkyllithium oligomer. Thus electrophilic reagents which are polar, and capable of strong interaction with the lithium atom sufficient to disrupt the bonding in the aggregate, appear to proceed with retention of configuration. Less polar substrates which must react with the oligomer directly give a mixture of products which favors inversion in most cases.

TABLE I

ISOMER DISTRIBUTIONS FROM THE HALOGENATION OF MENTHYL- AND *trans*-4-*t*-BUTYLCYCLOHEXYLLITHIUM[a]

Halogenating agent	Menthyllithium[b] 25°	−70°	Yield, %	4-*t*-Butylcyclohexyllithium[c] 25°	−70°	Yield, %
Cl_2	36/64[d]	50/50[d]	30	71/29[d]	69/31[d]	
Br_2	56/44	79/21	30	62/38	75/25	39
I_2	41/59	64/36		75/25	77/23	30
ICl[e]	Iodides[e]			Iodides[e]		
	42/50			23/27		34[e]
	Chlorides			Chlorides		
	0/8			18/32		
Pyridine–Br_2	20/80 (0°)		20	26/74 (0°)		6
$BrCH_2CH_2Br$	3/97		35	3/97		42

[a] All reactions were run in pentane solvent by addition of lithium alkyl to the appropriate halogenating agent. [b] See ref 1. [c] See ref 2. [d] Isomer distributions are reported as ratios of axial/equatorial halide isomers; thus the magnitude of the numerator reflects the extent of inversion of configuration in the process. [e] Isomer ratios for ICl reactions are reported on the basis of total halide formed. Yield is also based on total halide formed.

Other electrophilic substitution reactions which have previously been studied, including those of menthylmagnesium chloride in our laboratories, suggest that the generalizations made above are correct. Further studies in this area are in progress.

Experimental Section

Halides.—Menthyl and neomenthyl chlorides were prepared as described in paper II.[1] 4-*t*-Butylcyclohexyl chlorides were prepared by the method of Horner[21] using triphenylphosphine dichloride and 4-*t*-butylcyclohexyl alcohol (Aldrich, 80% *trans* isomer). The procedure was essentially the same as used for the preparation of neomenthyl chloride,[1] and resulted in approximately 26% yield of 4-*t*-butylcyclohexyl chloride containing 90 ± 5% *cis* isomer. An alternate preparative procedure utilizing phosphorus pentachloride was carried out in a three-neck flask with stirrer, Friedrichs condenser, and dropping funnel attached. The alcohol (0.434 mol) was added dropwise as a 2.0 *M* solution in pentane to a slight excess (10–20%) of PCl_5 (Eastman, practical grade) suspended in 200 ml of pentane. The mixture was stirred and refluxed for *ca.* 2.5–3 hr after the alcohol was added, then poured onto ice–sulfuric acid. The hydrocarbon layer was separated, washed with concentrated sulfuric acid several times until no color persisted, washed with water, and dried over anhydrous magnesium sulfate. The chloride was obtained by removal of the solvent and subsequent distillation, bp 78–80°, 9–10 torr. Typical yields were 48%, containing 20% *trans* and 80% *cis* isomer. Menthyl and 4-*t*-butylcyclohexyl chlorides were analyzed by nmr,[1] more often, by glpc using a 100 ft × 0.01 in. Golay column with di-*n*-butyl tetrachlorophthalate liquid phase (DBTCP). Column temperature was 94°, helium carrier flow was 10 ml/min. Injector temperature was varied and shown to be noncritical below 140°. Retention times (minutes) were menthyl (2.56), neomenthyl (2.50), *cis*- (3.65) and *trans*-4-*t*-butylcyclohexyl (4.35), respectively, for the chlorides.

4-*t*-Butylcyclohexyl bromide was prepared by the method of Eliel and Haber.[22] The product, obtained in 20% yield at 75–76° (8 torr) contained 80% *cis* isomer (τ 5.38) and 20% *trans* isomer (τ 6.08). Menthyl and neomenthyl bromides were prepared by the method of Horner. Approximately a 20% yield of product containing 76% menthyl (τ 6.10) and 24% neomenthyl (τ 5.38) isomers was obtained. Retention times of the bromides (minutes) on the DBTCP Golay column were menthyl (3.90), neomenthyl (3.70), *cis*- (6.14) and *trans*-4-*t*-butylcyclohexyl (7.52), respectively.

Iodides were not prepared other than by direct reaction of the alkyllithium with iodine. Identification of glpc retention times was made by preparative glpc collection of the suspected peaks from a 10 ft × 0.25 in. XF-1150 cyanosilicone column (20% on Chromosorb P, 30–60 mesh). Helium flow rate was 280 ml/min; injector temperature was lowered to 100° to minimize possible pyrolysis of the iodides; column temperature was 121°. Retention times (minutes) of the iodides under these conditions were *cis*- (33.3) and *trans*-4-*t*-butylcyclohexyl (38.4). Menthyl and neomenthyl iodides were analyzed on the DBTCP Golay column under the conditions mentioned above; retention times were 13.65 and 13.20 min, respectively. Chemical shifts of the methinyl proton of the iodides are menthyl (τ 6.04), neomenthyl (τ 5.32), *cis* (τ 5.25), and *trans* (τ 6.00).

Carbonation of Lithium Reagents.—The procedure was described in previous papers.[1,2]

Deuterolysis of Lithium Reagents.—An analyzed solution of the lithium reagent in pentane was transferred in a drybox to an apparatus consisting of a 25-mm lower tube with 24/40 ₸ outer joint at the top. The inner joint which fit into the lower part was connected to a three-way stopcock and had a side arm 14/35 ₸ outer joint below the stopcock. A stopcock adapter was fitted into this joint. After adding the lithium reagent solution to the 25-mm tube, the rest of the apparatus was assembled and

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[20] F. R. Jensen, L. H. Gale, and J. E. Rodgers, *J. Amer. Chem. Soc.*, **90**, 5793 (1968). Whether the product distributions are explained by torsional strain, as proposed by these authors, or by some other factor, is unimportant to our work. It is clear that the results shown in Table I are quite different from those obtained from typical cyclohexyl radical reactions with bromine and chlorine in which 1:1 ratios are observed.

[21] L. Horner, H. Oedinger, and H. Hoffmann, *Ann. Chim.*, **626**, 26 (1959).

[22] E. L. Eliel, and R. G. Haber, *J. Org. Chem.*, **24**, 143 (1959).

brought out of the drybox, being careful to have all stopcocks closed to the air. An excess of deuterium oxide (or deuterated alcohol) was placed in a bent tube with a 14/35 ₸ inner joint at the open end. This tube was attached to the stopcock side arm of the apparatus. The apparatus was cooled at the bottom with Dry Ice–acetone, and the deuterium oxide added quickly. The mixture was then allowed to warm slowly to room temperature. Analysis of the deuterated hydrocarbons was made by infrared techniques utilizing the C–D stretching bands.[3,23,24] The frequencies for axial and equatorial deuterium atoms occur at 2138 and 2167 cm^{-1}, respectively, for 3-deuterio-*p*-menthane and 2115–2135 and 2167–2184 for 1-deuterio-4-*t*-butylcyclohexane, respectively. The two C–D stretching vibrations were not resolved for the menthane isomers.

Reaction of Lithium Reagents with Trimethylsilyl Chloride.—An analyzed pentane solution of the lithium reagent was removed from the drybox in an erlenmeyer flask with a syringe cap. A stoichiometric quantity of chlorotrimethylsilane (redistilled, Pierce Chemical Co.) in ether (or pentane) was added. The flask was swirled in an ice bath during the addition. After approximately 1 hr (or 24 hr in the absence of ether) the reaction mixture was filtered to remove the lithium chloride precipitate. The filtrate was distilled to remove any excess trimethylsilyl chloride as well as the solvent. Analysis of the remainder of the solution was carried out on a 10 ft × 0.25 in. XF-1150 column at 125°, 240 ml/min flow of He. The suspected silane peaks were collected by preparative glpc from this column. Only small quantities of neomenthyltrimethylsilane and *cis*-4-*t*-butylcyclohexyltrimethylsilane were obtained and complete identification of these materials was never made. In the case of the *cis*-4-*t*-butylcyclohexyl compound, however, enough was collected by glpc to obtain an nmr spectrum which confirmed the assignment of retention times. Menthyltrimethylsilane was obtained by distillation at 125° (14 torr). The 100-MHz nmr resonance of the methinyl proton on the ring carbon bonded to silicon was characteristic of *axial* protons. The rotation of the compound was measured, $[\alpha]_D$ −32.4° (*c* 5.32, benzene). *trans*-4-*t*-Butylcyclohexyltrimethylsilane was collected from the XF-1150 column at 125°. Nmr again confirmed the methinyl proton to be *axial* by its splitting pattern. Approximately 85% of silane product was isolated from the reaction in ether–pentane solution after 1 hr at room temperature.

Chlorination of Lithium Reagents.—Crystalline lithium reagents were redissolved in *n*-pentane for these experiments if possible.[1,2] The solution was brought out of the drybox in a closed-off dropping funnel which was quickly fitted into one arm of a three-necked flask with magnetic stirrer inside. An argon inlet tube provided an inert blanket for the reaction atmosphere. The flask contained an excess of chlorine-saturated pentane. The lithium compound was added to the chlorine over an interval of about 5 min. Reactions were run at room temperature and at Dry Ice–acetone temperatures. In earlier runs, the chlorine–pentane was added to the solution of the lithium reagent; however, this procedure is not recommended since coupling between the alkyllithium and alkyl chloride is a complicating side reaction under these conditions, especially for bromides and iodides at room temperature. In the case of chlorinations, no difference in the isomer distribution of the chlorides formed was observed from the normal and inverse addition procedures. The chlorides were analyzed by glpc as described above, sometimes with no purification of the solutions at all. Isomer ratios were also determined by nmr immediately after the chlorination was complete. The reactions were also run in the dark, and no effect of light was noticed on the reaction products.

Bromination of Lithium Reagents.—The procedure was very nearly the same as for the chlorinations described above. Reactions were run with minimum exposure to light in most cases.

Iodination of Lithium Reagents.—The procedure was the same as for chlorinations and brominations described above. The effect of light on the alkyl iodides is very significant, and light exposure was minimized as much as possible.

Reactions of Lithium Reagents with 1,2-Dibromoethane.—The procedure consisted simply in adding alkyllithium solution to an excess of 1,2-dibromoethane in the drybox. The bromide isomers were analyzed by glpc as described above. In this case, as well as all other reactions, yields were determined by an internal standard method by glpc. Dodecane and decane were the most commonly used standards.

Bromination of Lithium Reagents with Pyridine–Bromine.—Pyridine was distilled from barium oxide. Bromine (18 mmol) and ~62 mmol of pyridine were mixed in a three-necked flask. The alkyllithium solution (8.37 mmol) was added over a period of about 7 min while cooling in an ice bath. The reaction mixture was stirred for approximately 25 min more, poured into a sulfuric acid–ice mixture (the hydrocarbon layer separated), and washed with concentrated sulfuric acid, then water, then $\mathrm{NaHCO_3}$, and finally water. The layer was dried over magnesium sulfate and analyzed by glpc as described above.

Reaction of Lithium Reagents with Iodine Monochloride.—Iodine monochloride was prepared by the procedure of Cornog and Karges.[25] The procedure was essentially the same as described above for reaction with chlorine. Analysis of the iodides and chlorides was carried out by glpc as described above.

Reaction of Lithium Reagents with Methyl Iodide.—An analyzed solution of the lithium compound in pentane was quickly mixed with methyl iodide in the drybox. An exothermic reaction occurs immediately in which the methyllithium precipitates. The precipitate was quickly filtered away, and the filtrate analyzed by nmr for the two isomeric iodides.

Reaction of Menthyllithium with Bromobenzene.—To a solution of freshly recrystallized menthyllithium in pentane was added a twofold excess of bromobenzene. A rapid, exothermic reaction occurred which resulted in the formation of a precipitate. The solid was quickly removed by filtration through a glass frit in a drybox, and the filtrate was analyzed by nmr. Integration of α-methinyl proton resonances of menthyl and neomenthyl bromide indicated a ratio of 85:15, respectively. A total yield of *ca.* 60% based on initial menthyllithium was determined by glpc with dodecane internal standard.

Registry No.—I, 18366-90-0; II, 18366-91-1.

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[23] E. J. Corey, R. A. Sneen, M. G. Danaher, R. L. Young, and R. L. Rutledge, *Chem. Ind.* (London), 1294 (1954).

[24] C. M. Selman, Ph.D. Thesis, North Texas State University, Denton, Texas, 1968.

[25] J. Cornog and R. A. Karges, *Inorg. Syn.*, **1**, 165 (1939).