ing of reagent gases for chemical ionization experiments has been described.

All samples were introduced into the source region of the mass spectrometer by direct insertion probe. An all glass probe (manufactured by Mass Spectrometer Accessories, College Station, Tex.), which has a separate heating and control system, was used in all experiments. Probe temperatures necessary for sample vaporization were 35-45°

8,9-Dehydro-2-adamantanol (1) was prepared by the sodium borohydride reduction of 8,9-dehydro-2-adamantanone (4) as described by Baldwin and Foglesong.²¹ However, an improved procedure for the synthesis of 4 was employed.²²

2-exo-Protoadamantenol (2). To 10 ml of an 80% aqueous acetone solution which was 0.05 M in perchloric acid was added 100 mg of 1. The solution was stirred at reflux for 18 hr and then diluted with 20 ml of water, neutralized with saturated sodium bicarbonate solution, and extracted with ether $(3 \times 30 \text{ ml})$. The combined ether extracts were washed with water and dried over anhydrous magnesium sulfate, and the solvent was evaporated at reduced pressure. Glpc analysis (10 ft \times 0.25 in, FFAP column, 190°, 60 ml/min of He) of the residue indicated a single component and pmr analysis (integration of the olefinic proton signals vs. chloroform as an internal standard) showed that the olefinic product was obtained in nearly quantitative yield. Pure 2 was isolated by glpc (above conditions) to give a white solid: mp 188-189°; pmr $(CDCl_3) \delta 6.45-5.9 \text{ (m, 2 H, olefinic protons), 3.71 [(br s, <math>W_{1/2} =$ 3.2 Hz, CH(OH)], 2.7-1.2 (m, 13 H); ir (CCl₄) 3630, 3350, 3035, 2920, 2865, 2850, 1460, 1430, 1365, 1210, 1175, 1150, 1100, 1060, 1050, 1030, 1015, 1000, 975, 945, 920, 900, and 700 cm⁻¹

Anal. Calcd for C10H14O: C, 79.96; H, 9.39. Found: C, 79.82; H, 9 27

The skeletal framework of 2 and the skeletal position and stereochemistry of the hydroxyl substituent in 2 were established by conversion of 2 to the known alcohol,²³ 2-exo-protoadamantanol (5). A solution of 40 mg of 2 in 25 ml of ethanol was stirred with 100 mg of 5% palladium on charcoal under an atmosphere of hydrogen for 24 hr. The reaction mixture was then diluted with 100 ml of pentane and filtered to remove the catalyst. The catalyst was washed with pentane (2 \times 20 ml) and the combined organic extracts were washed with several portions of water and then dried over anhydrous magnesium sulfate.

Evaporation of the solvent at reduced pressure provided an oily residue which glpc analysis (5 ft \times 0.25 in. FFAP column, 175°, 60 ml/min of He) showed contained a single component. Isolation of this compound by glpc (above conditions) gave pure 5, which was identified by comparison of its ir spectrum with that of an authentic sample.²³

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Reductive Arylation of Aromatic Hydrocarbons. I. Naphthalene and Anthracene¹

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Reductive phenylation of anthracene and naphthalene via treatment of the hydrocarbons with metals (sodium or potassium) in liquid ammonia and then with halobenzenes furnished 9-phenyl-9,10-dihydroanthracene and isomeric 1-phenyldihydronaphthalenes and 2-phenyldihydronaphthalenes in good yields. With lithium metal only the reduction of the hydrocarbon is obtained. A benzyne mechanism is proposed.

Metal-ammonia reduction and reductive alkylation of hydrocarbons have been widely used.² The structures of the dihydroaromatic products obtained by metal-ammonia reductions correlate to a remarkable degree with predictions of Hückel molecular orbital theory,³ and several hydrocarbons such as naphthalene,⁴ anthracene,^{2b} phenanthrene,⁵ chrysene,⁶ cycloheptatriene,⁷ fluoranthene,⁸ biphenyl,⁹ and terphenyl¹⁰ have been reduced to the anions and then alkylated. The reductive methylations of anthracene, benz[a] anthracene, and dibenz[a,h] anthracene occur

with regiospecificity to furnish the cis-dialkyldihydro derivatives.11

However, as far as we know, no attempt was made to perform a reductive arylation of these hydrocarbons. The recently discovered reaction of phenyl radical with hydrocarbons such as indene, fluorene, 1,3-pentadiene, and anethole¹² by the SRN1 mechanism¹³ to furnish the aryl-substituted hydrocarbons prompted us to investigate the possibility of phenylating aromatic hydrocarbons under reductive conditions, and we performed some reactions to try the

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reductive arylation of two hydrocarbons, anthracene and naphthalene.

Results and Discussion

When bromobenzene or chlorobenzene were added to a solution of anthracene dianion prepared from the reaction of anthracene with 2 equiv of potassium metal in liquid ammonia,^{2b} they reacted immediately, *before* the addition of potassium metal as electron source to form phenyl radicals,^{12,13} giving a mixture of 9,10-dihydroanthracene (40–55%), 9-phenyl-9,10-dihydroanthracene (35–45%), 9,9-diphenyl-9,10-dihydroanthracene (4–10%) and 9,10-diphenyl-9,10-dihydroanthracene (2–6%).

There are three possible mechanisms to explain this reaction. The first is direct nucleophilic displacement of halogen. This possibility has been rejected because aromatic nucleophilic substitution occurs very slowly if at all, with unactivated aromatic substrates.¹⁴

The second is electron transfer from the dianion to the halobenzene, giving the radical anion of the latter, which then decomposes to phenyl radical, and the reaction with the anion in the usual SRN1 mechanism^{12,13} (eq 1).

$$An^{2-} + PhX \longrightarrow An^{-} + PhX^{-}$$

$$PhX^{-} \longrightarrow Ph^{-} + X^{-}$$
(1)

The electron transfer reaction between dianions and neutral molecules is a known process.¹⁵ Iodobenzene and diphenyliodonium bromide gave this reaction with the acetonate anion in liquid ammonia,^{16,17} and the rate of decomposition of the former is dramatically increased by irradiation with near-uv lamps,¹⁶ whereas bromobenzene or chlorobenzene do not react without irradiation.¹⁶ Trimethylphenylammonium iodide and diethylphenyl phosphate also give phenyl radicals when treated with potassium metal¹⁷ or irradiated in liquid ammonia.¹⁶

If the first step in this reaction is an electron transfer, any one of the substrates cited above should give this reaction and also the same product distribution. However, trimethylphenylammonium iodide or diethylphenyl phosphate neither in the dark nor irradiated with 350-nm uv lamps gave phenylated products. This rules out the electron transfer mechanism.¹⁸ However, the addition of potassium metal to a mixture of anthracene dianion and trimethylphenylammonium iodide led to the formation of 9phenyl-9,10-dihydroanthracene in small yield (run 12, Table I) probably through an SRN1 mechanism.

The third is the benzyne mechanism. Lindow, Cortez, and Harvey demonstrated that the biphenyl dianion and anthracene dianion react with ammonia to give the monoanion and amide ions (eq 2), the proton addition is es-

$$An^{2-} + NH_3 \rightleftharpoons AnH^- + NH_2^-$$
(2)

sentially an irreversible process by experiments with deuterium exchange, and there are doubts whether these dianions can exist in ammonia at all.⁹

It is known that amide ion reacts with halobenzenes to give *o*-halophenyl anion, which then decomposes to benzyne,^{19a} which in turn could be trapped by anthracene mono- or dianion, giving the observed products (Scheme I). Reactions of benzyne with carbanions are well known.^{19b}

9,9-Diphenyl-9,10-dihydroanthracene and 9,10-diphenyl-9,10-dihydroanthracene are products from 9-phenyl-9,10-dihydroanthracene anion and benzyne, and represent a double arylation.

Since the formation of benzyne requires a reaction medium basic enough to form the *o*-halophenyl anion, addition of lithium metal to form the dianion, instead of potassium metal, will reduce the basicity of the solution owing to the



insolubility of the lithium amide in ammonia,²⁰ which will shift the equilibrium of eq 2 to the right. As expected, when lithium metal was used to form anthracene dianion in ammonia, and chlorobenzene was added, no reaction occurred (run 5, Table I).

In the reaction of anthracene dianion with a fivefold excess of chlorobenzene, there is no increase in the yield of phenylation (run 3, Table I), and when anthracene dianion was half neutralized by adding 1 equiv of solid ammonium bromide to form anthracene monoanion, and chlorobenzene was added, no phenylation products were found (run 6, Table I).

From the observations discussed above, we conclude that the anthracene dianion is basic enough to be in equilibrium with amide ion, and form benzyne from halobenzenes, and the latter reacts with anthracene anion to form the products observed.

Further evidence to demonstrate that the reaction occurs via a benzyne mechanism is the lack of the reaction of 2,6dimethylchlorobenzene with naphthalene dianion, owing to the impossibility of this substrate forming benzyne.²¹

All these reactions were carried out after 5 min of the formation of the anion of the reduced species (mono- or dianion), which is recognized by the formation of the red color. When the halobenzene was added 60 min after the red color had been formed, no phenylated products were formed (run 7, Table I). When the halobenzene was added 15 min after the red color had been formed, a decrease in the yield was observed (run 8, Table I). These phenomena are not fully understood and are discussed in the reductive phenylation of naphthalene.

Reductive Phenylation of Naphthalene. Metal-ammonia reduction of naphthalene and its derivatives is a well-known reaction, and the reduction proceeds through naphthalene radical anion and dianions.² It is generally assumed that the position of protonation by a suitable proton donor is governed by the charge distribution in these intermediates species as provided by esr data²² or quantum chemical calculations.^{3,23}

The reduction of naphthalene with lithium metal in liquid ammonia is very rapid and the initially formed product is 1,4-dihydronaphthalene, undergoing amide-catalyzed

Table I
Reactions of Anthracene Dianion with Monosubstituted Benzenes in Liquid Ammonia

Run	Anthracene, mol	K metal, mol	PhX	Mol	Product yield, % ^{e,f}			
					DHA 4	9-PDHAb	9,9-DPDHA¢	9, 10-DPDHAd
1	0.104	0.208	Cl	0.112	54	36	4	2
2	0.120	0.300	Cl	0.132	38	43	11	6
3	0.128	0.260	Cl	0.64	35	40	16	6
4	0.140	0.086	C1	0.048	40	41	8	4
5	0.040	0.280 ⁿ	Cl	0.152	100			
6 ⁱ	0.072	0.144	Cl	0.072	100			
7	0.052	0.108	$C1^{j}$	0.052	100			
8	0.048	0.101	$C1^k$	0.048	78	17		
9	0.192	0.404	Br	0.212	41	44	9	3
10	0.100	0.200	⁺ NMe ₃	0.100	100			
11	0.048	0.104	⁺ NMe ₃	0.0521	100			
12	0.056	0.112	⁺ NMe ₃	0.056 ^m	95	5 <i>"</i>		
13	0.024	0.052	DEPP°	0.024	100			

^a 9,10-Dihydroanthracene. ^b 9-Phenyl-9,10-dihydroanthracene. ^c 9,9-Diphenyl-9,10-dihydroanthracene. ^d 9,10-Diphenyl-9,10-dihydroanthracene. ^e Yields determined by glpc. ^f Aniline and biphenylamine were detected in small amounts (1-6%). ^g Na metal. ^h Li metal. ⁱ After the formation of anthracene dianion, 0.072 mol of NH₄Br was added. ^f PhCl was added after 60 min of formation of anthracene dianion. ^k PhCl was added after 15 min of formation of anthracene dianion. ^l Irradiated with 350-nm uv lamps. ^m 0.080 mol of K metal was added to produce phenyl radicals. Other products detected but not quantified: benzene, aniline, and biphenylamine. ^o Diethylphenyl phosphate ester.

 Table II

 Reactions of Naphthalene Dianion with Monosubstituted Benzenes in Liquid Ammonia

					Product yield, % ^{e, f}					
Run	Naphthalene, mol	K metal, mol	PhX	Mol	DHN ¢	1-PDHN ^b	2-PDHNC	DPDHN ¢		
1 ^{<i>e</i>}	0.044	0.092	Cl	0.044	33 + 7	32 ∓ 6	25 ∓ 3	3 7 1		
2 ^{<i>h</i>}	0.048	0.100	Br	0.048	35	30	28	2		
3 ⁱ	0.040	0.080	Cl	0.040	100					
4	0.040	0.100 ^{<i>j</i>}	Cl	0.040	100					
5	0.028	0.056	[*] NMe ₃	0.028	100					
6	0.042	0.084	2,6-DMCB ^k	0.042	100					

^a Dihydronaphthalenes. ^b Isomeric 1-phenyldihydronaphthalenes; no attempt was made to identify them. ^c Isomeric 2-phenyldihydronaphthalenes; no attempt was made to identify them. ^a Diphenyldihydronaphthalenes. ^e Yields determined by glpc. ^f Aniline and biphenylamine were detected in small amounts. ^g Average of four runs. ^h Average of two runs. ⁱ Two runs, at 15 and 60 min after the formation of the naphthalene dianion. ^f Li metal. ^k 2,6-Dimethylchlorobenzene, recovered almost quantitatively.

isomerization to 1,2-dihydronaphthalene in about 1 hr at -33° .²⁴

When naphthalene dianion was formed by the reaction of potassium metal and naphthalene in liquid ammonia, and chlorobenzene or bromobenzene were added, a complex mixture of products was found, mainly 1,2-dihydronaphthalene and 1,4-dihydronaphthalene (33-35%), 1phenyldihydronaphthalenes (30-32%), and 2-phenyldihydronaphthalenes (25-28%). By gas-liquid partition chromatography technique, there were several peaks with similar retention times, probably due to isomeric 1-phenyldihydronaphthalenes and 2-phenyldihydronaphthalenes. No attempt to isolate them was made, and the crude products of phenylation were dehydrogenated to 1-phenylnaphthalene and 2-phenylnaphthalene and characterized as such.

When lithium metal was used instead of potassium metal to form naphthalene dianion, no reaction occurred (run 4, Table II), and when trimethylphenylammonium iodide was used instead of chlorobenzene or bromobenzene, no reaction occurred either (run 5, Table II).

All these facts suggest, as in the reductive phenylation of anthracene, that a benzyne mechanism occurs. As a means to demonstrate absolutely the formation of benzyne as a route to phenylated products, we turned our attention to arylation with 2,6-dimethylchlorobenzene, which cannot form an aryne with a strong base.²¹

As anticipated, it was unreactive with the naphthalene dianion under the same experimental conditions as chloroor bromobenzene, and it was recovered unchanged (run 6, Table II).

From these observations, we conclude that the reaction of alkali metals with naphthalene in liquid ammonia gives naphthalene dianion, which is protonated by the ammonia in the sense of eq 2, and the amide ion precipitates (lithium amide) or gives benzyne (potassium amide) with halobenzenes, which reacts with naphthalene anion, giving 1-phenyldihydronaphthalenes and 2-phenyldihydronaphthalenes in almost the same ratio, independently of the halobenzene used, probably owing the presence of two isomeric anions.

It is known that 1,4-dihydronaphthalene is formed first and then by an amide-catalyzed reaction gives 1,2-dihydronaphthalene.²⁴ In an attempt to try to obtain selective phenylation of naphthalene, once it was formed, 1 hr was allowed to pass at -33° before the addition of the halobenzene, but no phenylated products were found. In the previReductive Arylation of Naphthalene and Anthracene

This rapid decay of the reactivity of the naphthalene anion is not fully understood, but it could be due to the slow protonation of the naphthalene monoanion by ammonia to give the reduced and neutral dihydronaphthalene and amide anions (eq 3).

 $Naph^{2-} + NH_3 \rightleftharpoons NaphH^{-} + NH_2^{-}$ (fast) (2)

$$NaphH^{-} + NH_3 \rightleftharpoons NaphH_2 + NH_2^{-} (slow)$$
 (3)

Kinetic and equilibrium studies of the protonation of the dihydronaphthalene anion and dihydroanthracene anion are being developed in our laboratories to test this idea.

Experimental Section

General. Boiling and melting points have not been corrected. Nmr spectra were recorded on a Varian T-60 nuclear magnetic resonance spectrometer with CCl₄ as solvent and all spectra are reported in parts per million relative to TMS (δ). All ir spectra are recorded on a Beckman IR-8 spectrophotometer. Ultraviolet spectra were recorded on a Beckman DB-6 spectrophotometer. Thin layer chromatography was performed on silica gel plates. Gas chromatographic analyses were performed on a F & M biomedical gas chromatograph, Model 400, with flame ionization detector and yields were determined by peak area with a 6 ft \times $\frac{3}{16}$ in. column packed with 4% silicon rubber SE-30 on 60-80 Chromosorb P

Reagents. Naphthalene (Eastman), anthracene (Fluka), chlorobenzene (Fluka), and bromobenzene (Fluka) were commercially available and were used as received. Trimethylphenylammonium iodide and diethylphenyl phosphate ester were available from previous work.¹⁷ 2,6-Dimethylchlorobenzene was obtained by a Sandmeyer reaction of 2,6-dimethylaniline (K & K Laboratories): bp 181-184° (720 mm) (lit.²⁵ bp 185-187°); nmr δ 2.32 (s, 6 H) and 7.12 (s, 3 H). Alkali metals were cut in small pieces and washed free of oil with dried ether or pentane immediately before addition to reaction mixtures. Liquid ammonia was dried with sodium metal and distilled under nitrogen into the reaction flask.

Reductive Phenylation of Anthracene. A procedure for reductive phenylation of anthracene is representative. The reaction was performed in a three-neck round-bottom flask fitted with a Dry Ice-isopropyl alcohol condenser, stirred by a magnetic stirrer and constantly swept by a slow stream of dry nitrogen. To distilled liquid ammonia (350 ml) potassium metal (0.101 mol) was added and solid anthracene (0.048 mol) was added to the blue solution. After the blue color of the alkali metal had changed to a dark orange-red color (about 4-8 min), bromobenzene (0.053 mol) was added drop by drop from a separatory funnel. At the end the color changed to a dark violet. After 10 min of reaction, solid ammonium chloride was then added to quench the reaction, followed by 150 ml of diethyl ether, and the ammonia was allowed to evaporate. The ether extract was washed with water and dried over anhydrous Na₂SO₄. A small portion of the ether extract was analyzed by glpc. The ether was evaporated from the rest of the ether layer, and the residue was fractionately sublimed. The products isolated were 9,10-dihydroanthracene (60–70°, 1 Torr), mp 106–108° (lit.²⁶ mp 89-90°), nmr spectrum δ 3.86 and 3.94 (2 H), 5.14 (1 H), and an authentic sample,27 and 9-phenyl-9,10-dihydroanthracene (110-115°, 1 Torr), recrystallized from ethanol, mp 88-90° (lit.28 mp 89-90°), nmr spectrum δ 3.86 and 3.94 (2 H), 5.14 (1 H), and ca. 7.2 (13 H) [lit.²⁸ (CS₂ as solvent) δ 3.70 and 3.88 (2 H) and 5.04 (1 H)]. A sample was dehydrogenated to 9-phenylanthracene by heating with sulfur at 190-200° during 30 min, and the residue was crystallized from ethyl alcohol, mp 150-152° (lit.²⁹ mp 154-155°).

A mixture of 9,9-diphenyl-9,10-dihydroanthracene and 9,10diphenyl-9,10-dihydroanthracene sublimed at 150-160° (1 Torr), determined by nmr and glpc analysis. 9,10-Diphenyl-9,10-dihydroanthracene was isolated pure by fractional recrystallization from diethyl ether, mp 188–193° (lit.³⁰ mp 194–195°), and by nmr analysis there were two isomers, cis and trans, δ 5.25 and 5.33 (2 H) and 7.13 and 7.22 (18 H). After the ether was distilled off, 9,9-diphenyl-9,10-dihydroanthracene was obtained, nmr δ 3.86 (2 H) and ca.7.1 (18 H)

Attempt to Phenylate Anthracene Dianion with Trimethylphenylammonium lodide. The procedure was similar to the phenylation using halobenzenes, except that solid trimethylphenylammonium iodide was added. The reactions were carried out in the dark, or irradiated with two 350-nm 250-W high-pressure mercury lamps (Philips, Model HPT) during 1 hr. The reactions were quenched and the work-up was similar to the previous one, but no phenylated products were found.

Potassium Metal as Catalyst. The procedure was similar to the method described previously.¹² Once trimethylphenylammonium iodide was added to the anthracene dianion in ammonia, potassium metal was added in small pieces. After all the K metal was added, the reaction was quenched by adding ammonium chloride and the work-up was similar to those of the other reactions. 9-Phenyl-9,10-dihydroanthracene was obtained in 5% yield by glpc.

Reductive Phenylation of Naphthalene. The procedure was similar to the reductive phenylation of anthracene. To 250 ml of dry ammonia, K metal (23 mmol) was added and solid naphthalene (11 mmol) was added to the blue solution. When the blue color of the alkali metal had changed to a dark red color (about 3-7 min) and after 5 min with this color, chlorobenzene (11 mmol) was added and the reaction mixture was quenched by adding ammonium chloride after 10 min of reaction. The ammonia was allowed to evaporate and the residue was treated with water and twice extracted with diethyl ether. The ether extract was washed with water and dried over anhydrous Na₂SO₄. A small portion of the ether was analyzed by glpc. The ether was evaporated and the residue was treated with powdered sulfur (11 mmol) and heated to 230-240° for 0.5 hr.³¹ The black residue was extracted with ether, and a small portion was analyzed by glpc. The ether was evaporated and vacuum distilled, giving naphthalene, 1-phenylnaphthalene (210-230°, 67 Torr), and 2-phenylnaphthalene (230-250°, 67 Torr). Pure 1-phenylnaphthalene was obtained by column chromatography on silica gel, using light petroleum as solvent, giving a waxy, white solid, uv (cyclohexane) λ_{max} 228 and 285 nm [lit.³² uv (cyclohexane) λ_{max} 228 and 285 nm]. 2-Phenylnaphthalene was purified by recrystallization in ethanol, giving a white solid, mp 102-103° (lit.³³ mp 101-102°), uv (cyclohexane) λ_{max} 250 and 285 nm [lit.³⁴ uv (cyclohexane) λ_{max} 250 and 285 nm].

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Registry No.-Naphthalene, 91-20-3; anthracene, 120-12-7; chlorobenzene, 108-90-7; bromobenzene, 108-86-1; trimethylphenylammonium iodide, 98-04-4; diethyphenylphosphate ester, 2510-86-3; 2,6-dimethylchlorobenzene, 6781-98-2; 9-phenyl-9,10dihydroanthracene, 13577-28-1; cis-9,10-diphenyl-9,10-dihydroanthracene, 52196-17-5; trans-9,10-diphenyl-9,10-dihydroanthracene, 52196-18-6; 9,9-diphenyl-9,10-dihydroanthracene, 7477-39-6; 1-phenylnaphthalene, 605-02-7; 2-phenylnaphthalene, 612-94-2.

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Stereoselective Organometallic Alkylation Reactions, III. "Ate" Complex Addition to Cyclic and Bicyclic Ketones¹

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The stereochemistry of addition of a variety of "ate" complexes with such ketones as 4-tert-butylcyclohexanone, 3,3,5-trimethylcyclohexanone, norcamphor, and camphor has been studied. The reaction of LiAl(CH₃)₄ and LiAl(i-C4H9)3CH3 with 4-tert-butylcyclohexanone in benzene, diethyl ether, tetrahydrofuran, and dimethoxyethane results in predominant axial attack to form equatorial alcohol (via methylation), regardless of reactant ratio or reaction time. However, the reaction of other "ate" complexes such as $LiB(CH_3)_4$ and $Li_n M(CH_3)_{2+n}$ compounds (where M = Mg and Zn and n = 1, 2, or 3) with 4-tert-butylcyclohexanone yields predominantly equatorial attack in diethyl ether. Reaction of all ate complexes studied with 3,3,5-trimethylcyclohexanone yields 100% axial alcohol. Reaction of norcamphor and camphor with all ate complexes studied yields 95% endo alcohol and 99% exo alcohol, respectively, regardless of reactant ratio.

Ate complexes are the result of interaction between an electron-deficient metal alkyl and a Lewis base.² Trimethylaluminum, for example, exists as a dimer with two methyl groups bridge bonded in such a way that the coordination about the aluminum atom is tetrahedral.³ In ether solution the weak methyl bridge bonds are broken in favor of ether solvation of the trimethylaluminum. If methylithium is added to the solution, the ether molecule is replaced by a methyl carbanion to form the ate complex $LiAl(CH_3)_4$. Basically these are simply acid-base reactions where the Lewis acid $[Al(CH_3)_3]$ reacts with a base (e.g., ether or CH_3Li) to form a salt. In general, the tendency toward

$$\begin{array}{c} CH_{3} \\ CH_{3} \\ CH_{3} \end{array} \xrightarrow{CH_{3}} Al \xrightarrow{CH_{3}} CH_{3} \xrightarrow{2CH_{3}Li} 2(CH_{3})_{3}Al \cdot OEt_{2} \\ CH_{3} \\ CH_{3} \xrightarrow{2CH_{3}Li} 2LiAl(CH_{3})_{4} \end{array}$$
(1)

ate complex formation and the stability of the complex depend to a large degree on the particular metals involved and to a lesser degree on the ligand size and charge. For example, the tendency of the adducts $LiM(C_6H_5)_3$ to dissociate into phenyllithium and $M(\mathrm{C}_6\mathrm{H}_5)_2$ increases in the order $LiBe(C_6H_5)_3 < LiZn(C_6H_5)_3 < LiMg(C_6H_5)_3 <$ $LiCd(C_6H_5)_3 < LiHg(C_6H_5)_3$. In general, the smaller the central metal atom and the more electropositive the group I metal the more stable is the adduct. Indeed, in the above series the largest metal, mercury, shows no tendency to form an adduct.

No reports concerning either the mechanism or stereochemistry of ate complex addition to ketones has appeared in the literature. Since the central metal atom of ate complexes such as LiAl(CH₃)₄ or Li₂Mg(CH₃)₄ do not have

available orbitals for complexation with a carbonyl group as do $(CH_3)_3Al$ and $(CH_3)_2Mg$, there is reason to believe that the mechanism and hence stereochemistry of reaction should be different. In addition it was felt that since lithium is capable of complexing with carbonyl compounds, possibly at complexes of the type $Li_n M(CH_3)_{2+n}$ might react by complexation of the lithium atom with the carbonyl oxygen atom. Such possibilities, in addition to recent re-



ports concerning the composition of ate complexes in solution,⁴ have prompted us to investigate these compounds as stereoselective alkylating agents.

Experimental Section

Materials. Methyllithium was obtained from Foote Mineral Co. and was used without further purification. Analysis of CH₂Li gave CH₃:Li ratios ranging from 0.95:1 to 1:1 and essentially no halide was detected. Solutions of CH3Li were refrigerated in serum capped bottles and their concentrations were checked prior to use. Dimethylmagnesium was prepared from dimethylmercury by reaction with Dow Chemical Co. doubly sublimed magnesium turnings.⁵ Trimethylborane was prepared by reaction of BF₃. $O(C_2H_5)_2$ with methylmagnesium bromide. The trimethylborane was distilled from the reaction vessel and collected at Dry Ice-acetone temperature. Dimethylzinc was prepared by reaction of methylmagnesium bromide with anhydrous zinc chloride followed by distillation of the dimethylzinc under reduced pressure. Potassium tert-butoxide was prepared by reaction of potassium metal with excess tert-butyl alcohol. Excess tert-butyl alcohol was removed