When the tubes had come to constant temperature, they were removed individually from the bath at fixed times and quenched by cooling. The concentration of undecomposed initiator was determined from the intensity of the 370-mμ band. Experiments generally were run to 90% decomposition. The results, given in Table I, were obtained by least squares. Where decomposition had been extensive, N_2 evolution was obvious when the tube was opened, and the odor of isobutyl acetate was prominent.

Lithium Aluminum Methide as an Alkylating Agent[1]

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The aluminum tetramethide anion has been characterized by proton magnetic resonance and its use as an alkylating agent has been studied. Reaction with benzaldehyde leads to the utilization of two of the available methyl groups, whereas with aliphatic aldehydes only one methyl group is utilized. Ketones undergo a very slow alkylation giving low yields of tertiary alcohols. Acid chlorides react to give methyl ketones with the utilization of only 1 equiv. of the reagent. Esters, nitro compounds, nitriles, and sulfonate esters do not undergo reaction with lithium aluminomethide (lithium aluminum methide).

The first complex aluminum alkide, lithium aluminomethide (LAM), was apparently first prepared by Hurd[2] in 1948. LAM was described as a stable solid at 80° but was very reactive to moisture. Baker and Sisler prepared sodium and lithium aluminoethide in 1953 and studied the reactions of the reagents with several inorganic compounds.[3] Sodium aluminoethide was also prepared in 1959 as an intermediate in the synthesis of triethylaluminum[4] and Ziegler and co-workers studied the addition of this compound to olefins.[5] Walter prepared lithium aluminoethide by reaction of diazomethane with lithium aluminum hydride and observed the formation of diethyl ketone and propionic acid on treatment with carbon dioxide.[6]

Similar boroalkide complexes have also been described in the literature. Schlesinger and Brown have described lithium trimethylethylboron as a fairly stable solid.[7] Blitzen and Pearson prepared lithium boroethide which proved to be a very stable compound which could be sublimed at 160–170° without decomposition.[8] These authors reported that sodium boroethide was a good alkylating agent for producing tertiary alcohols from ketones; however, no experimental details were given. Ashby has observed that complex boroalkides are capable of reducing acids and ketones and the alkylation of carbonyl compounds.[9]

Although Hurd[2] indicated the possible utility of complex alumino- and boroalkides in organic synthesis in 1948 the only results appearing in the literature concern the complex boroalkides. It seemed of interest to study the potential utility of a complex aluminoalkide, namely LAM, as an alkylating agent. This article reports the results of this investigation.

Lithium aluminomethide is readily prepared by the addition of an ethereal solution of trimethylaluminum to a cooled ethereal solution of methyllithium. The complex was characterized by its proton magnetic resonance (p.m.r.) spectrum which displayed a singlet at +63 c.p.s. relative to internal tetramethylsilane. Mixtures of trimethylaluminum and methyllithium in which the former is in excess display a single p.m.r. peak intermediate between pure ethereal trimethylaluminum (+55 c.p.s., 2.0 *M* in diethyl ether) and LAM indicating a rapid exchange of methyl groups in the system. Similar chemical shifts changes are observed for the α-protons of the ether solvent owing to changes in the extent of complexing of the ether. Addition of an excess of methyllithium (+116 c.p.s., 1.69 *M* in diethyl ether) to LAM solutions results in two peaks in the p.m.r. spectrum which remain constant in position with changes in the relative amounts of the two reactants present. Both peaks correspond to the peak positions for pure LAM and methyllithium. This latter data would indicate that the dissociation of LAM to methyllithium and trimethylaluminum, followed by possible exchange, is a relatively slow process if it occurs at all. This is pertinent in considering the alkylation reactions involving LAM.

Ethereal solutions of LAM hydrolyze rather slowly in the presence of water or aqueous base, the rate of the hydrolysis decreasing markedly with the extent of hydrolysis. Hydrolysis with 10% sulfuric acid is initially quite vigorous and requires approximately 10 min. for completion at 0°. The extent of reaction in the alkylation reactions was determined by gas evolution measurements during hydrolysis. These results agreed closely with the gas–liquid chromatographic analytical results. Ethereal solutions of LAM undergo air oxidation unless protected from oxygen. The p.m.r. spectra of ethereal solutions left open to the air develop additional peaks which correspond to peaks formed if one adds methanol to pure ethereal LAM. Reactions of oxidized LAM solutions with benzoyl chloride produced substantial amounts of methyl benzoate.

The alkylation of benzaldehyde appears to result in the utilization of only two of the available four methides. The reactions appear to be quite rapid at 25° in ether. When the alkylation is carried out in refluxing tetrahydrofuran (66°), 2 equiv. of methide are utilized, but the yield of 1-phenylethanol decreases. This is primarily due to the incursion of a hydride transfer

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[1] This work was supported by the Petroleum Research Fund of the American Chemical Society, Grant No. PRF 1225-A1,3.

[2] G. T. Hurd, *J. Org. Chem.*, **13**, 711 (1948).

[3] E. B. Baker and H. H. Sisler, *J. Am. Chem. Soc.*, **75**, 5193 (1953).

[4] Bergwerksgesellshaft Hibernia Akt. Ges., British Patent 822,971 (Nov. 4, 1959); *Chem. Abstr.*, **54**, 14125*i* (1960).

[5] K. Ziegler, H-G. Gellert, K. Zosel, E. Holzkamp, J. Schneider, M. Soll, and W-R. Kroll, *Ann.*, **629**, 121 (1960).

[6] H. A. Walter (to the Monsanto Chemical Co.), U. S. Patent 2,864,842 (Dec. 16, 1958); *Chem. Abstr.*, **53**, 7014*e* (1959).

[7] H. J. Schlesinger and H. C. Brown, *J. Am. Chem. Soc.*, **62**, 3429 (1940).

[8] S. M. Blitzen and T. H. Pearson (to the Ethyl Corp.), U. S. Patent 2,944,084 (July 5, 1960); *Chem. Abstr.*, **54**, 24398*f* (1960).

[9] E. C. Ashby (to the Ethyl Corp.), U. S. Patent 3,007,970 (April 28, 1958); *Chem. Abstr.*, **56**, 6000*b* (1962).

from the 1-phenylethoxyaluminomethide to benzaldehyde giving benzyl alcohol and acetophenone, the latter undergoing a slow alkylation to give phenyldimethylcarbinol. The results of the alkylation of benzaldehyde are presented in Table I.

TABLE I

REACTION OF LAM WITH VARIOUS SUBSTRATES

Substrate	Mole ratio of LAM/substrate	Reaction time, hr.	Temp., °C.	Product	% yield
Benzaldehyde	1	1	25	$C_6H_5CHOHCH_3$	26
Benzaldehyde	2	1	25	$C_6H_5CHOHCH_3$	59
Benzaldehyde	1	1	65[a]	$C_6H_5CHOHCH_3$[b]	40
n-Octaldehyde	1	1	25	$CH_3(CH_2)_6CHOHCH_3$	19
n-Butyraldehyde	1	1	25	$CH_3(CH_2)_2CHOHCH_3$	18
Isobutyraldehyde	1	1	25	$(CH_3)_2CHCHOHCH_3$	21
Pivalaldehyde	1	1	25	$(CH_3)_3CCHOHCH_3$	19
Acetophenone	1	1 min.	25	$C_6H_5COH(CH_3)_2$	Trace
Acetophenone	1	1	25	$C_6H_5COH(CH_3)_2$	10
Cyclohexanone	1	1	25	1-Methylcyclohexanol	15
Cyclohexanone	2	5	25	1-Methylcyclohexanol	45
2-Octanone	1	1 min.	25	$CH_3(CH_2)_5COH(CH_3)_2$	Trace
2-Octanone	1	1	25	$CH_3(CH_2)_5COH(CH_3)_2$	10
Benzoyl chloride	1	1	25	$C_6H_5COCH_3$[c]	22
Benzoyl chloride	2	1	25	$C_6H_5COCH_3$[c]	30
Benzoyl chloride	4	1	25	$C_6H_5COCH_3$[c]	36
Phenylacetyl chloride	1	4	25	$C_6H_5CH_2COCH_3$	22

[a] In tetrahydrofuran. [b] The product mixture also contained low yields of benzyl alcohol, acetophenone, and phenyldimethylcarbinol. [c] Contained low yields of phenyldimethylcarbinol.

Alkylation of aliphatic aldehydes results in the utilization of only one methide. Treatment of *n*-butyraldehyde, isobutyraldehyde, *n*-octylaldehyde, or pivaladehyde with LAM gives 15–20% yields of alkylation products (see Table I).

Ketones react slowly with LAM to give poor yields of tertiary alcohols. It appears that only 1 equiv. of methide reacts. In addition to alkylation, proton abstraction, with the formation of methane, occurs with ketones.

Acid chlorides react with LAM to give methyl ketones, again with the utilization of only one methide. The reaction appears to be quite rapid and leads to an immediate precipitation of lithium chloride. Increasing the ratio of LAM to chloride does not improve the yields substantially as with the alkylation of aldehydes. The trimethylaluminum generated in the reaction of the acid chloride, to give the methyl ketone and lithium chloride, appears to interfere in the reaction. The subsequent alkylation of the intermediate ketone is much slower, but nevertheless small quantities of tertiary alcohol are formed. Table I includes the results from the reactions of benzoyl and phenylacetyl chlorides with LAM.

Esters, nitriles, and nitro compounds fail to react with LAM. An attempt to displace a *p*-toluenesulfonate group by a methyl group, similar to the lithium aluminum hydride reduction of tosylates, also met with failure. In all of these reactions the starting materials were recovered in excellent yield.

Experimental

Preparation of Lithium Aluminomethide (LAM).—Trimethylaluminum (2.00 *M* in diethyl ether from Ethyl Corp.) was slowly added to a cooled solution of methyllithium (1.69 *M* in diethyl ether from Foote Mineral Co.)[10] maintained under nitrogen until an equal number of moles of each reagent was present. The reagent was placed in a rubber septum stoppered bottle and stored in the refrigerator. Aliquots were removed by means of a syringe.

Proton Magnetic Resonance Spectra of Trimethylaluminum–Methyllithium Mixtures.—Aliquots of trimethylaluminum (2.00 *M* in ether) and methyllithium were mixed and the p.m.r. spectra were recorded on a Varian HR-60 spectrometer using tetramethylsilane as an internal standard. The composition of the solutions is reported as the ratio of the total number of methyl groups contributed by trimethylaluminum to the total number of methyl groups contributed by methyllithium (ratio). These results are presented in Table II.

TABLE II

P.M.R. SPECTRA OF TRIMETHYLALUMINUM–METHYLLITHIUM SOLUTIONS

Ratio	C.p.s. relative to TMS
Trimethylaluminum	+55
10:1	+57.9
6:1	+59.3
3:1 (LAM)	+63
2:2	+64, +115
1:4	+64, +115
Methyllithium	..., +116

Alkylation Reactions Using LAM.—To a solution of 0.01 mole of substrate in 25 ml. of diethyl ether maintained under a nitrogen atmosphere was added the LAM solution (the quantities of LAM added with respect to the substrate are included in Table I). The reaction mixture was stirred for the indicated length of time (Table I) and hydrolyzed by the careful addition of 5 ml. of 10% sulfuric acid. The gas evolved during the hydrolysis was measured and the amount of residual methide was calculated. After hydrolysis the reaction mixture was transferred to a separatory funnel. The reaction flask was washed with 5 ml. of water and 20 ml. of ether, the washings being added to the separatory funnel. The organic layer was washed with water and dried over magnesium sulfate. The ether was fractionally distilled and the residues were analyzed by gas–liquid chromatography on various columns depending on the starting material and products. The yields were calculated by the addition of a known amount of an internal standard and conversion of the area ratios to absolute weights with predetermined relative response factors. The results are presented in Table I.

The alkylation of benzaldehyde in refluxing tetrahydrofuran at 66° was accomplished by the prior addition of dry tetrahydrofuran and distillation of the diethyl ether. The benzaldehyde, dissolved in tetrahydrofuran, was then added and the reaction mixture was refluxed.

The work-up procedure for the attempted alkylation of nitro compounds varied from that described above. The hydrolyzed mixture was made basic and then extracted with ether to recover any basic materials that may have been formed.

The gas–liquid chromatographic analysis were carried out using a 20% Carbowax on firebrick column for experiments involving the aldehydes and acid chlorides, a 20% THEED on firebrick column for the ketones, and a 20% silicone rubber on firebrick column for the acid chlorides.

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(10) The authors wish to thank the Foote Mineral Co. for providing generous amounts of methyllithium.