the water before addition of the diazonium salt and the copper(I) catalyst. A β-naphthol test was done on all the reactions to ascertain that all the diazonium salt had decomposed. When the reaction was complete, as indicated by a negative β-naphthol test, the reaction mixture was extracted three times with 150 ml of methylene chloride. If the reaction was performed in acidic solution, the combined organic extract was washed with saturated $NaHCO_3$ and water before drying. The combined organic extracts were then dried over anhydrous magnesium sulfate and concentrated at reduced pressure.

Copper(I) Hydride.[7,8]—Copper(I) hydride was prepared by the reaction of lithium aluminum hydride with copper(I) iodide in pyridine; however, the resulting CuH was impure and stable when exposed to air. In a procedure reported by Whitesides[8] using di*iso*butylaluminum hydride and copper(I) chloride in place of $LiAlH_4$ and CuI, a pure product of CuH was obtained. The material, which was light brown, decomposed in about 10 min after being dried from ether. This, however, was enough time for us to carry out experiments.

2-Iodobenzophenone.[18,19]—*o*-Iodobenzoyl chloride (Fisher, reagent grade) 50 g (0.188 mol), in 200 ml of dry benzene was gradually treated with 28 g (0.211 mol) of powdered anhydrous aluminum chloride, and the mixture was refluxed for 2 hr. After hydrolysis of the complex, *o*-iodobenzophenone along with other products was obtained as a nearly colorless liquid (34 g, 59%), bp 143° (0.3 mm), which solidified and gave needles, mp 32.5°, from hexane.

2,2′-Dibenzoylbiphenyl.—*o*-Iodobenzophenone, 20 g (0.065 mol), and 18 g (0.284 g-atom) of electrolytic copper (Fisher) in 40 ml of dimethylformamide were heated under reflux for 2 hr. The product was taken up in chloroform, the solvents were removed, and the solid residue was recrystallized from cyclohexane, yielding 9.0 g (76%) of 2,2′-dibenzoylbiphenyl as white needles, mp 167°.

Registry No.—**1,** 342-62-1; **2,** 119-61-9; **3,** 117-99-7; **4,** 486-25-9; **5,** 24018-00-6; salt 1, 14057-91-1; salt 2, 37847-53-3; salt 3, 15418-29-8; salt 4, 37821-06-0; salt 7, 37821-07-1; copper(II) acetate monohydrate, 6046-93-1; 2-iodobenzophenone, 25187-00-2.

Reaction of Acetaldehyde with Mono- and Binuclear Organoaluminum Compounds at Low Temperature

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Received September 11, 1972

Studies of the reaction of pentaalkyldialuminum alkali metal oxide and its nitrogen and sulfur analogs with acetaldehyde at −78, −20, and 0° are reported and compared with AlR_3 alone and with mononuclear complexes $AlR_3\cdot Do$. AlR_3 gave addition and reduction products as the primary reaction and some secondary reaction products. The reactivity of $AlR_3\cdot Do$ decreased with respect to both of the primary and secondary reactions with increase in the strength of the complex. Pentaalkyldialuminum complexes have high reactivity concerning the primary reaction, but have very low activity for the secondary reactions. The results can best be understood by a bimetallic cyclic transition state. With $[R_2AlZLi]\cdot[AlR'_3]$, R′ addition and R addition occurred simultaneously, indicating a slow alkyl exchange process through a bridging alkyl.

Our recent works on the polymerization catalyst revealed that the reaction products from trialkylaluminum with alkali metal hydroxide[1-4] and lithium amide[2,3,5] in a molar ratio of 2:1 gave highly isotactic polyacetaldehyde with desired properties.[4] Extensive studies on the syntheses in the pure state[6] and nmr spectroscopy[7] on the structures in solution have elucidated that the organoaluminum compound produced can be represented as a series of binuclear complexes of the formula $[R_2AlZM]\cdot[AlR_3]$ with high complex stability when Z = O or NR′, in which R_2AlZM serves as a donor and AlR_3 as an acceptor.

In order to study both the active species for initiation and the side reactions by the organoaluminum catalyst in the polymerization, detailed studies on the reaction with acetaldehyde were carried out at −78 (polymerization temperature), −20, and 0° (higher than the ceiling temperature of the polymerization). The binuclear organoaluminum compound was found to exhibit a characteristic reactivity of the AlR group as compared with trialkylaluminums and their mononuclear complexes. Our results may contribute also to fill the gaps in our knowledge of the reactions of organoaluminum reagents with carbonyl compounds,[8-10] in which reaction intermediates involving two metals have been presumed for a few cases.[11-13] On the basis of the reaction of acetaldehyde with $[R_2AlZM]\cdot[AlR'_3]$ new information on the intramolecular alkyl–alkyl and "alkyl–alkoxyl" exchange reactions is also obtained.

Results and Discussion

Trialkylaluminums.—On the basis of the results with $AlEt_3$, $AlMe_3$, and Al-*i*-Bu_3 (Table I), the reaction process of acetaldehyde can be summarized in Scheme I, which involves primary and secondary reactions.[14] In the primary reaction AlR_3 reacts with acetaldehyde in two ways; widely known Grignard addition (a) and reduction (b). The organoaluminum alkoxides derived from the primary reaction acts as the reagent for

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(2) H. Tani, T. Araki, N. Oguni, and T. Aoyagi, *ibid., Part B-4*, 97 (1966).

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(5) H. Tani and N. Oguni, *ibid., Part B-3*, 123 (1965).

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SCHEME I

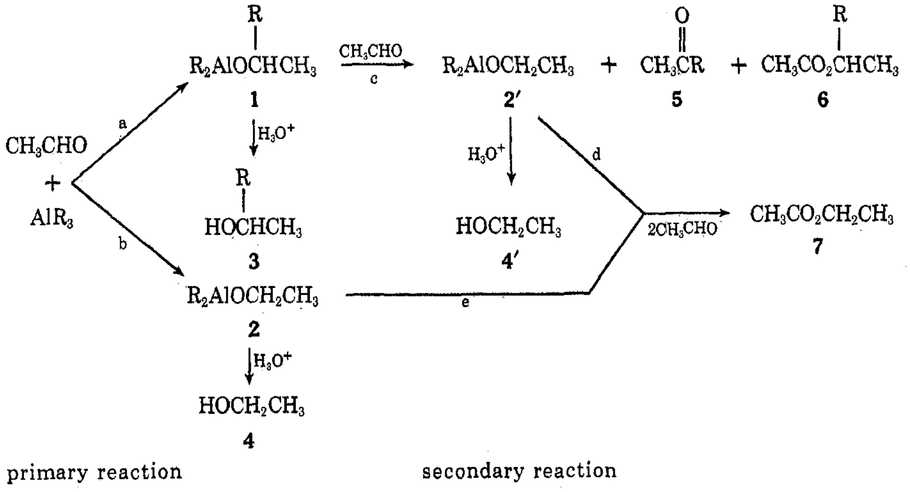

TABLE I

REACTION OF ACETALDEHYDE WITH AlR_3 AND Et_2AlOR[a]

Registry no.	Organoaluminum	Temp, °C	Time, hr	CH_3CHO concn[b]	Reaction product, mol/mol organoaluminum[c] 4	7	5	3	6	CH_3CHO recovered
97-93-8	$AlEt_3$	−78	2[d]	5	<0.1	0.10	0	0.91	0	4.2
	$AlEt_3$	−20	2[e]	5	0.5	0.83	<0.1	0.78	~0.2	2.7
	$AlEt_3$	0	24	5	0.72	1.6	0.43	0.13	0.35	
7062-93-3	Et_2AlO-*sec*-Bu	−78	20	3	0	<0.1	0	0[f]	0	3.2
	Et_2AlO-*sec*-Bu	−20	20	3	0.87	0.96	<0.1	−0.38[g]	0.23	1.4
	Et_2AlOEt	−20	20	3	0.1[f]	0.41	0	0	0	2.3
75-24-1	$AlMe_3$	−78	24	5	0	0	0	0.16	0	4.7
	$AlMe_3$	−20	5[h]	5	<0.1	0.63	<0.1	1.4	<0.1	2.7
	$AlMe_3$	0	5[i]	5	0.29	0.75	0.17	1.2	0.10	
100-99-2	Al-*i*-Bu_3	−78	1	5	0.51	<0.1	0	0.28	0	4.0
	Al-*i*-Bu_3	−20	20	5	0.70	2.1	~0.2	<0.1	~0.2	1.5

[a] Toluene (5 ml) and organoaluminum compound (4.7×10^{-4} mol) were used. [b] Mol/mol of organoaluminum compound. [c] Formation of paraldehyde did not exceed the amount yielded in the control experiment. [d] The results are almost identical at 1 hr, except for somewhat lower yield of **7**. [e] At 1 hr, yields of **4** and **7** were less than 50% of these values, and yield of **3** was *ca.* 15% higher than the value in this table. [f] 1.0 molar equiv of alcohols which was present originally in Et_2AlOR' was excluded. [g] Minus value means the consumption of *sec*-BuOAl group originally present in Et_2AlO-*sec*-Bu. [h] At 1 hr, yield of **7** was *ca.* 0.2 but yield of **3** was nearly the same as the value in this table. Compounds **4** and **5** were not observed at shorter reaction times. [i] At 1 hr, **4** (0.16), **7** (0.10), **3** (1.3), and **6** (<0.1) were observed.

the secondary reactions (Meerwein–Ponndorf–Verlay reduction, Oppenauer oxidation, and Tishchenko reaction) analogously to aluminum trialkoxides.[15]

At −78° the primary reactions occur preferentially with $AlEt_3$, $AlMe_3$, and Al-*i*-Bu_3. The addition reaction is highly predominant for $AlEt_3$[16] or $AlMe_3$. The pronounced difference in the reactivity between $AlEt_3$ and $AlMe_3$ can be related with the difference in their dimer stabilities.[17] Al-*i*-Bu_3, known as an effective reducing agent,[18] gives reduction product predominantly over addition product by a factor of 1.8. For the secondary reactions, not negligible amounts of **7** were solely detected for $AlEt_3$ and Al-*i*-Bu_3.

At −20°, the secondary reactions giving **4′**, **5**, **6**, and especially Tishchenko reaction product **7** become important. The results obtained with Et_2AlO-*sec*-Bu or Et_2AlOEt indicate that the complicated reaction products are derived from these alkoxide species. The secondary reactions are further promoted at 0°.

Mononuclear Complexes of AlR_3.—The complexes of AlR_3 (R = Et and Me) with organic donors were purified by distillation or sublimation and confirmed to be monomeric cryoscopically. The heats of formation of complexes $AlR_3 \cdot Do$ (Do: organic donor) have been determined by Bonitz[19] and Hendrickson, *et al.*[20] (see Table VI). The reactivity of each series of $AlR_3 \cdot Do$ with acetaldehyde is consistent with the complex stability of $AlR_3 \cdot Do$. Diethyl etherates react similarly to uncomplexed AlR_3. Tetrahydrofuranates are inactive for addition reactions at −78° but they give both of the primary and secondary reaction products at −20°, *e.g.*, **4** (<0.1 mol/mol $AlEt_3 \cdot THF$), **7** (0.61), and **3** (0.56). For aminates, the primary and subsequently

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(17) A. W. Laubengayer and W. F. Gilliam, *J. Amer. Chem. Soc.*, **63**, 477 (1941).

(18) K. Ziegler, K. Schneider, and J. Schneider, *Angew. Chem.*, **67**, 425 (1955).

(19) E. Bonitz, *Ber.*, **88**, 742 (1955).

(20) C. H. Hendrickson, D. Duffy, and D. P. Eyman, *Inorg. Chem.*, **7**, 1047 (1968).

TABLE II

REACTION OF ACETALDEHYDE WITH $[R_2AlZM]\cdot[AlR_3]^a$

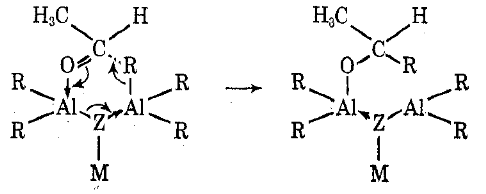
					Reaction products, mol/mol of organoaluminum^c			
Registry no.	Organoaluminums	Temp, °C	Time, hr	CH_3CHO concn^b	**4**	**7**	**3**	CH_3CHO recovered
37916-23-7	$[Et_2AlOLi]\cdot[AlEt_3]$	−78	24	5	0	0	1.28	3.7
	$[Et_2AlOLi]\cdot[AlEt_3]$	−20	24	5	0	0	1.59	3.3
	$[Et_2AlOLi]\cdot[AlEt_3]$	0	24	5	0	0	1.95	3.2 ± 0.2
	$[Et_2AlOLi]\cdot[AlEt_3]$	−20	24	100	<0.1	<0.1	1.26	
	$[Et_2AlOLi]\cdot[AlEt_3]$	0	1	100	<0.1	<0.1	1.32	
	$[Et_2AlOLi]\cdot[AlEt_3]^d$	0	20	100	1.9	3.90	0.10	
37916-24-8	$[Et_2AlONa]\cdot[AlEt_3]$	−78	24	3	<0.1	0	0.50	2.4 ± 0.2
	$[Et_2AlONa]\cdot[AlEt_3]$	−20	24	3	<0.1	0	1.33	1.6 ± 0.2
	$[Et_2AlONa]\cdot[AlEt_3]^e$	−20	24	100	0.73	<0.1	0.69	
37916-25-9	$[Me_2AlOLi]\cdot[AlMe_3]$	−78	24	5	0	0	0.78^f	3.9
	$[Me_2AlOLi]\cdot[AlMe_3]$	−20	24	5	0	0	0.86	3.9
	$[Me_2AlOLi]\cdot[AlMe_3]$	0	24	5	0	0	1.07	
37916-26-0	$[i\text{-}Bu_2AlOLi]\cdot[Al\text{-}i\text{-}Bu_3]^g$	−78	24	5	0.80	0	0.36	4.0
	$[i\text{-}Bu_2AlOLi]\cdot[Al\text{-}i\text{-}Bu_3]^h$	−20	24	5	1.1	0	0.42	3.0
37916-27-1	$[Et_2AlNPhLi]\cdot[AlEt_3]$	−78	20	5	0	0	1.94	
	$[Et_3AlNPhLi]\cdot[AlEt_3]$	−20	20	5	0	0	2.27	
	$[Et_2AlNPhLi]\cdot[AlEt_3]^i$	−20	20	100	∼0.2	3.7	0.2	
37916-28-2	$[Et_2AlSNa]\cdot[AlEt_3]$	−78	24	5	<0.1	0	0.53	
	$[Et_2AlSNa]\cdot[AlEt_3]$	−78	24	10	0.55	<0.1	0.41	
	$[Et_2AlSNa]\cdot[AlEt_3]$	−20	24	5	0.27	<0.1	0.91	
	$[Et_2AlSNa]\cdot[AlEt_3]^i$	−20	24	100	1.26	3.45	∼0.2	

[a] Toluene (5 ml) and organoaluminum (4.7×10^{-4} mol) were used. [b] Mol/mol of organoaluminum. [c] Formation of paraldehyde did not exceed the amount obtained by the control experiment. The products **5** and **6** were not detected or otherwise noticed. [d] Formations of ethyl methyl ketone (∼0.2) and *sec*-BuOAc (0.48 mol/mol of organoaluminum) were detected. [e] Formation of ethyl methyl ketone (<0.1) was observed. [f] Yield of **3**: 0.48 (12 min), 0.63 (1 hr), and 0.69 (2 hr). [g] Yield of **3** was almost unchanged from 12 min to 24 hr, but yield of **4** increased: 0.45 (12 min) and 0.72 (1 hr). [h] Almost the same results were obtained at 0°. [i] Formations of ethyl methyl ketone and *sec*-BuOAc (∼0.2 each) were detected.

the secondary reactions are completely inhibited at the temperatures studied.[21,22] It is reasonable to assume that the reactions involve the following ligand exchange process, and a four-coordinated complex whose ligand cannot be substituted for acetaldehyde is inactive. The coordinating ability of acetaldehyde to AlR_3 can be estimated to be comparable with (or slightly lower than) tetrahydrofuran.

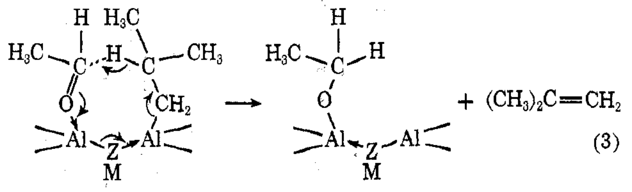
$$R_3Al\cdot Do \underset{-\,CH_3CHO}{\overset{+\,CH_3CHO}{\rightleftharpoons}} R_3Al\cdot OCHCH_3 + Do \qquad (1)$$

Pentaalkyl Dialuminum Compounds.—This series of compounds can best be represented as a complex of type $[R_2AlZM]\cdot[AlR_3]$.[6,7] In contrast to the organic donors, the Al-containing donors (R_2AlZM) suppress only the secondary reactions (Table II). $[R_2AlZM]\cdot[AlR_3]$ with R = Me, Et and Z = O, NPh was found to be a good reagent to give addition products, and the amount of the reaction products is almost saturated in 2 hr (Figure 1 and footnote of Table II). These results imply that the structure of the bimetallic complex is suitable for the primary reactions but not for the secondary reactions. Since we have already shown that $[R_2AlZM]\cdot[AlR_3]$ can exist as an unassociated state in nonpolar media,[6] and that an electron-donor molecule can coordinate preferentially with the Al atom in the R_2AlZM moiety,[7] the six-membered cyclic (eq 2) and eight-membered cyclic intermediates (eq 3) are highly



(2)

addition reaction (R = Me, Et, *i*-Bu)



(3)

reduction (*i*-Bu derivatives)

plausible for addition and reduction, respectively. Increase in the inhibiting effect of the organic donors added to $[Et_2AlOLi]\cdot[AlEt_3]$ (Table III) was in agreement with the order of increase in the strength of the base. This effect clearly indicates coordination of the aldehyde with the organoaluminum complex to be responsible for the reaction.

Further two factors can be considered to interpret the facts that the yield of the addition product by $[R_2AlZM]\cdot[AlR_3]$ at −78° is higher than that by the corresponding AlR_3, and that more than one of five AlR groups is readily consumed. Firstly, coordination of the R_2AlZM facilitates the Al^{+}–R^{-} localization in the AlR_3 moiety. Secondly, the monoalkoxide obtained by the primary reaction can be isomerized intramolecularly into a structure adequate for further addition or reduction. In this paper the latter is denoted as

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(21) The reaction of $AlEt_3\cdot NEt_3$ with acetaldehyde depends upon the concentration of the system. At extremely high concentrations a complicated reaction including aldol condensation is observed (ref 23).

(22) The complexes $R_3Al\cdot OPPh_3$ show stability similar to the aminates for the reaction with acetaldehyde (ref 24).

(23) Y. Nakano, M. S. Thesis, Osaka University, 1967; H. Tani, T. Araki, and Y. Nakano, Abstract of Papers, 13th Annual Meeting of Polymer Science, Kobe, Japan, 1967, p 43.

(24) K. Lee, Ph.D. Thesis, Osaka University, 1970; H. Tani, T. Araki, and K. Lee, Abstract of Papers, 13th Annual Meeting of Polymer Science, Kobe, Japan, (1967), p 42.

TABLE III

REACTION OF ACETALDEHYDE WITH $[Et_2AlOLi]\cdot[AlEt_3]$ IN THE PRESENCE OF DONOR COMPOUNDS[a]

Donor	Donor/ organo- aluminum, mol/mol	Temp, °C	sec-BuOH formed,[b] mol/mol of organoaluminum
Et_2O	1[c]	−78	0.99
Et_2O	1	−20	1.51
THF	1[d]	−78	0.89
THF	1	−20	1.18
NEt_3	1[e]	−78	0.53
NEt_3	2	−78	0.05
NEt_3	5	−78	0
NEt_3	1	−20	0.57

[a] Toluene (5 ml) and $[Et_2AlOLi]\cdot[AlEt_3]$ (4.7×10^{-4} mol) were used. Concentration of acetaldehyde: 5 mol/mol $[Et_2AlOLi]\cdot[AlEt_3]$. Reaction time: 24 hr. [b] Any of other reaction products were not detected. [c] 1.1 molar equiv of *sec*-BuOH was formed at $Et_2O/[Et_2AlOLi]\cdot[AlEt_3]$ ratio = 5. [d] Yield of *sec*-BuOH was almost unchanged at 1 hr. [e] Yield of *sec*-BuOH was gradually increased from 0.22 (12 min) with increase of the time.

"alkyl/alkoxyl" exchange reaction. This process becomes prominent as the temperature increased or when the bond angle of Al–Z→Al becomes smaller (compare Al–O→Al with Al–N→Al).

The secondary reactions with $[R_2AlOM]\cdot[AlR_3]$ or $[R_2AlNPhM]\cdot[AlR_3]$ were detectable only at extremely high concentration of acetaldehyde at higher temperature. In contrast, $[Et_2AlSNa]\cdot[AlEt_3]$ gave the secondary reaction products more readily even under milder conditions. The facile occurrence of the products can be related with high tendency of the complex to dissociate into its moieties;[6] $[Et_2AlSNa]\cdot[AlEt_3] \rightleftarrows Et_2AlSNa + AlEt_3$ or $[Et_2AlSNa]\cdot[AlEt_3] + CH_3CHO \rightarrow [Et_2AlSNa]\cdot[Et_2AlO\text{-}sec\text{-}Bu] \rightleftarrows Et_2AlSNa + Et_2AlO\text{-}sec\text{-}Bu$. These results suggest that the secondary reactions are due to the dissociated moieties[25] of the complexes, especially AlR_3 or R_2AlOR' in the monometallic states. Further kinetic evidence will be necessary before more can be asserted about the monometallic process. The order of stability of the complex deduced is in the decreasing order of $Z = O \geq NPh \gg S$. The ionic property of M (by altering from Li to Na) does not affect the complex stability significantly. Et_2AlOLi or $Et_2AlNPhLi$ freed from $AlEt_3$ was confirmed not to form under various conditions any reaction products detectable by gas chromatography.

Intramolecular Alkyl/Alkyl and Alkyl/Alkoxyl Exchanges.—A previous nmr study[7] has indicated the existence of rapid alkyl/alkyl exchange processes in the binuclear complex containing a Li atom (at >60°). The reaction product of acetaldehyde with $[R_2AlZM]\cdot[AlR'_3]$, which was prepared[6] by complexation of R_2AlZM with AlR'_3, is a mixture of R- and R'-addition products (Table IV), indicating the existence of a slow alkyl/alkyl exchange process in addition. For *i*-Bu derivatives, the addition and reduction products are formed. The $\gamma_{R',R}$ values, defined as a ratio of AlR' to AlR groups reacted with acetaldehyde, vary with the reaction temperature, the complexation temperature, and aging period of the complex. Except for the complexes containing the *i*-Bu group which has decreased reactivity owing to its steric factor, the product of the AlR' group predominates as expected from the assumption made in eq 2. On the basis of the reaction data, the predominant species of the complex, prepared at −78° and aged for 1 hr, can be suggested as shown in Table V.

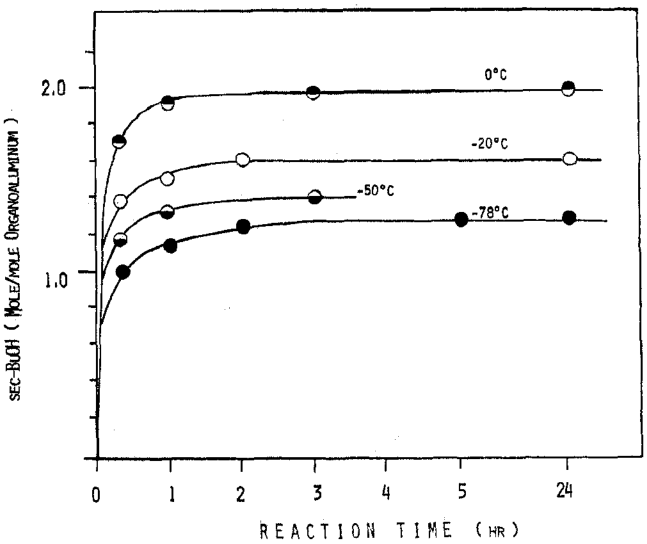
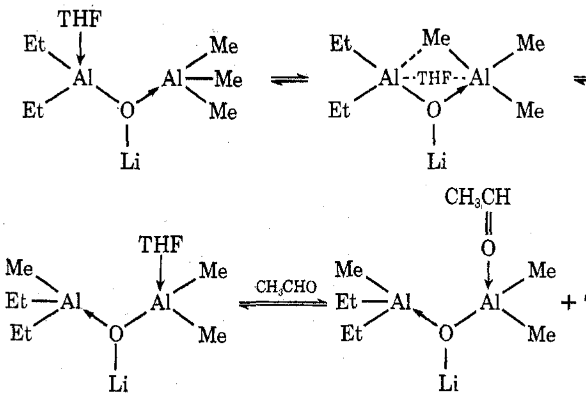


Figure 1.—Time dependence of the formation of *sec*-butyl alcohol by $[Et_2AlOLi]\cdot[AlEt_3]$ at various temperatures: toluene, 5 ml; $[Et_2AlOLi]\cdot[AlEt_3]$, 4.7×10^{-4} mol; CH_3CHO/organoaluminum, 5 mol/mol.

Since the number of alkyl groups consumed is higher than one per mole (at higher reaction temperature it reaches 2–3), an "alkyl/alkoxyl" exchange process must also be considered.[28] For the oxygen derivatives the exchange process appears not to be important at −78°[29] but it is observable at −20°. For the nitrogen derivative, the "alkyl/alkoxy" exchange occurs more rapidly at −78°, partly due to the decreased bond angle of Al–N→Al.

When an equimolar amount of THF (a donor with Lewis basicity comparable with acetaldehyde) is coor-



(4)

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[25] Examination of Et_2AlSNa (freed from $AlEt_3$) revealed that it can give ethyl acetate at −20° at low acetaldehyde concentration without forming ethanol. The remarkably high yield of ethyl acetate by $[Et_2AlSNa]\cdot[AlEt_3]$ is probably due to this factor in addition to the species AlR_3 and/or R_2AlOR'. Ethyl acetate formation without Al alkoxide species seems to proceed by a mechanism other than Tishchenko reaction. Other examples have been observed with $Et_2AlOAlEt_2$ (ref 26) and with the hydrolysate of $AlEt_3$ by aqueous KOH solution (ref 27). For convenience we denote it "direct dimerization."

[26] T. Araki, T. Aoyagi, N. Ueyama, T. Aoyama, and H. Tani, *J. Polym. Sci., Part A-1*, in press.

[27] T. Aoyagi, T. Araki and H. Tani, *Makromol. Chem.*, in press.

[28] For convenience, the notation is used to distinguish from the alkyl/alkyl exchange process. In practice, a rotation around an Al–O→Al bond followed by exchange of alkyl groups also affords a similar result.

[29] Elimination of inert gas from the reaction system resulted in enhanced "alkyl/alkoxyl" exchange for some unclarified reason.

TABLE IV

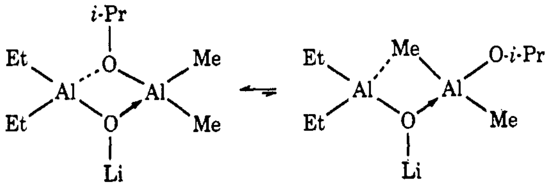
REACTION OF ACETALDEHYDE WITH $[\mathrm{R_2AlZLi}]\cdot[\mathrm{AlR'_3}]$[a]

Preparation and aging of organoaluminums		Reaction	Reaction products, mol/mol organoaluminum[b]				
Temp, °C	Time, hr	Temp, °C	$\mathrm{CH_3CHOHR}$	$\mathrm{CH_3CHOHR'}$	$\mathrm{CH_3CH_2OH}$	Total	$\gamma_{\mathrm{R',R}}$[c]
			$[\mathrm{Et_2AlOLi}]\cdot[\mathrm{AlMe_3}]$ (37916-29-3)[i]				
−78	1	−78	0.32	0.75	0	1.07	2.3[d]
−78	9	−78	0.44	0.86	0	1.30	2.0
−78	48	−78	0.43	0.79	0	1.22	1.9[e]
−78	1	−20	0.40	0.72	0	1.12	1.8
−78	1	0	0.47	0.88	0	1.35	1.7
0	1	−78	0.48	0.71	0	1.19	1.5
40	1	−78	0.53	0.71	0	1.24	1.3
40	9	−78	0.65	0.64	0	1.29	1.0
80	1	−78	0.53	0.71	0	1.24	1.3
			$[\mathrm{Me_2AlOLi}]\cdot[\mathrm{AlEt_3}]$ (37916-30-6)				
−78	1	−78	0.35	0.82	0	1.17	2.3[f]
−78	1	−20	0.50	1.04	0	1.54	2.1
−78	1	0	0.71	1.10	0	1.81	1.6
			$[\mathrm{Et_2AlOLi}]\cdot[\mathrm{Al}\text{-}i\text{-}\mathrm{Bu_3}]$ (37916-31-7)				
−78	1	−78	0.58	0.13	0.25	0.96	0.7
−78	1	−20	0.68	0.18	0.43	1.29	0.9
			$[\mathrm{Et_2AlNPhLi}]\cdot[\mathrm{AlMe_3}]$ (37916-32-8)				
−78	1	−78	0.51	1.07	0	1.58	2.1
−78	1	−20	0.54	1.29	0	1.83	2.4
			$[\mathrm{Et_2AlNPhLi}]\cdot[\mathrm{Al}\text{-}i\text{-}\mathrm{Bu_3}]$ (37916-33-9)				
−78	1	−78	1.20	0	0.44	1.64	0.4
−78	1	−20	1.20	0	1.50	2.70	1.3
			$[\mathrm{Et_2AlOLi\cdot THF}]\cdot[\mathrm{AlMe_3}]$ (37916-34-0)				
−78	1	−78	0.26	0.18	0	0.44	0.7
−78	1	−20	0.52	0.70	0	1.22	1.4
			$[\mathrm{Et_2AlOLi}]\cdot[\mathrm{AlMe_3\cdot THF}]$				
−78	1	−78	0.21	0.18	0	0.39	0.9[g]
−78	1	−20	0.43	0.53	0	0.96	1.2
			$[\mathrm{Et_2AlOLi}]\cdot[\mathrm{AlMe_3}]\cdot\mathrm{THF}$				
−78	1	−78	0.18	0.35	0	0.53	1.9
−78	9	−78	0.16	0.17	0	0.33	1.1
−78	48	−78	0.21	0.05	0	0.26	0.2
			$[\mathrm{Me_2AlOLi}]\cdot[\mathrm{AlEt_3\cdot THF}]$ (37916-35-1)				
−78	1	−78	0.09	0.23	0	0.32	2.5
−78	1	−20	0.26	0.79	0	1.05	3.0
			$[\mathrm{Et_2AlOLi}]\cdot[\mathrm{Me_2AlO}\text{-}i\text{-}\mathrm{Pr}]$[h] (37916-36-2)				
−78	48	−78	0	Trace	0	Trace	
−78	48	−20	Trace	Trace	0	Trace	
−78	48	0	Trace	Trace	0	Trace	

[a] Toluene (5 ml) and organoaluminum (4.7×10^{-4} mol) were used. Acetaldehyde concentration: 5 mol/mol of organoaluminum. Reaction time: 20 hr. [b] Any of other reaction products was not observed. [c] Ratio of R′ to R groups consumed in the reaction with acetaldehyde. [d] Time dependence of the reaction/time (hr), R addition, R′ addition, and $\gamma_{\mathrm{R',R}}$ are given: 0.5, 0.28, 0.62, 2.2; 1, 0.35, 0.70, 2.0; 4, 0.36, 0.71, 2.0. [e] Time dependence of the reaction (see *d*): 0.5, 0.29, 0.61, 2.1; 1, 0.40, 0.80, 2.0; 5, 0.40, 0.79, 2.0. [f] Time dependence of the reaction (see *d*): 0.2, 0.28, 0.86, 3.1; 1, 0.36, 0.90, 2.5. [g] Time dependence of the reaction (see *d*): 0.2, 0.18, 0.15, 0.8; 0.5, 2.0, 0.17, 0.9; 5, 2.0, 0.18, 0.9. [h] The amount of *i*-PrOH corresponding to the *i*-PrO group which was present in the organoaluminum was not included. [i] Registry number.

dinated with $[\mathrm{Et_2AlOLi}]\cdot[\mathrm{AlMe_3}]$ prior to addition of acetaldehyde, the $\gamma_{\mathrm{Me,Et}}$ value decreases from 2 to 0.2 during a long aging period. This indicates that the rate of the alkyl/alkyl exchange process has been decreased by the addition of THF as observed in the nmr study.[7] Total consumption of the alkyl groups at −78° is lowered to less than one-half of the case without THF. In $[\mathrm{Et_2AlOLi}]\cdot[\mathrm{AlMe_3\cdot THF}]$, $[\mathrm{Et_2AlOLi\cdot THF}]\cdot[\mathrm{AlMe_3}]$, and $[\mathrm{Me_2AlOLi}]\cdot[\mathrm{AlEt_3\cdot THF}]$, methyl addition is considerably decreased as compared with ethyl addition, indicating that methyl bridging can compete with donation of THF more strongly than ethyl bridging.

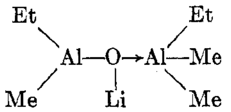
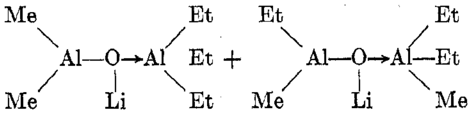
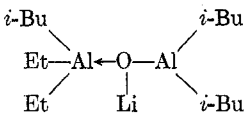
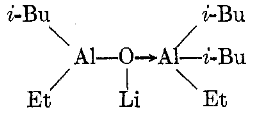
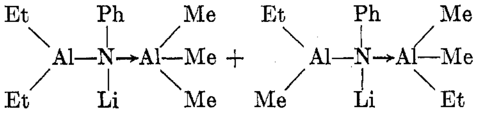
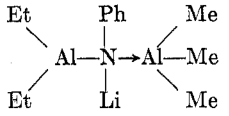
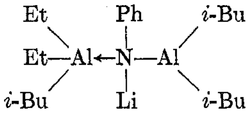
It is interesting to note that, although the "alkyl/alkoxyl" exchange process can be seen when $[\mathrm{Et_2AlOLi}]\cdot[\mathrm{AlMe_3}]$ is directly reacted with acetaldehyde at higher temperature, the complex $[\mathrm{Et_2AlOLi}]\cdot[\mathrm{Me_2AlOiPr}]$ is virtually inactive to further addition reaction. This



(5)

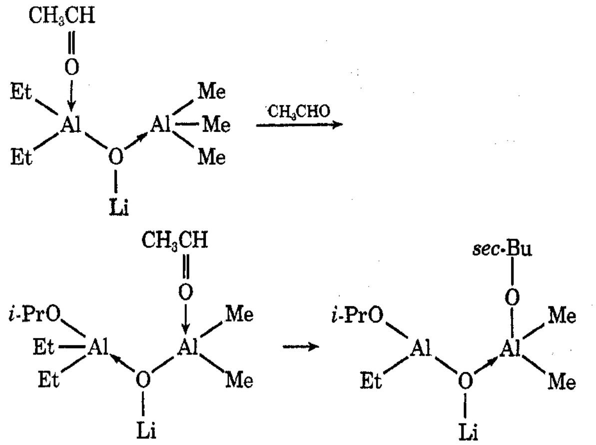
TABLE V

SUGGESTED SPECIES OF $[R_2AlZLi]\cdot[AlR'_3]$ PREDOMINANT AT THE TEMPERATURE OF REACTION WITH ACETALDEHYDE

Type of complex	Structure of predominant species: −78°	Structure of predominant species: Higher temperature
$[Et_2AlOLi]\cdot[AlMe_3]$		Randomly distributed
$[Me_2AlOLi]\cdot[AlEt_3]$		Randomly distributed
$[Et_2AlOLi]\cdot[AliBu_3]$		
$[Et_2AlNPhLi]\cdot[AlMe_3]$		
$[Et_2AlNPhLi]\cdot[AliBu_3]$		Randomly distributed

observation implies the presence of a stable intermediate just like a stable dimer of R_2AlOR'[30] in the "alkyl/alkoxyl" exchange process.

With an excess mole of acetaldehyde, some of the organoaluminum molecules would be coordinated by the aldehyde simultaneously to the first formation of the alkoxyl group, and subsequently further addition would take place (eq 6).



(6)

The four-membered ring opens preferentially at the Al–OR side, not at the Al–OLi side. Thus, two kinds of solids $[Et_2AlOLi]\cdot[Et_2AlO\text{-}sec\text{-}Bu]$ could be obtained, one of which is less soluble and monomeric, regardless of its concentration in benzene solution. The other form is highly soluble and monomeric in dilute solution. The former has lower catalyst activity than the latter. The details of the study will be published elsewhere.

Experimental Section

Experiments were carried out under an argon atmosphere.

Materials.—Acetaldehyde was prepared from paraldehyde and purified as previously described.[27] Solvents were purified as described in another paper.[6]

Organoaluminums.—$AlMe_3$, $AlEt_3$, and Al-*i*-Bu_3 were obtained from a commercial source (Ethyl Corp.) and purified by single distillation under reduced pressure. Et_2AlO-*sec*-Bu, bp 52.5–53.0° (3×10^{-3} mm), and Et_2AlOEt, bp 40.5–45.0° (0.1×10^{-2} mm), were prepared from equimolar reactions of $AlEt_3$ with *sec*-BuOH and EtOH, respectively, and purified by distillation *in vacuo*. $AlR_3\cdot Do$ complexes were prepared from equimolar reactions of AlR_3 with corresponding organic Lewis bases, which are listed in Table VI. Preparation and purification of the binuclear organoaluminum complexes were carried out as described in another paper.[6] $[Et_2AlOLi]\cdot[AlMe_3\cdot THF]$, $[Et_2AlOLi\cdot THF]\cdot[AlMe_3]$, and $[Me_2AlOLi]\cdot[AlEt_3\cdot THF]$ were prepared by equimolar complexation of the corresponding moieties in toluene. The complexation temperature and aging periods are included in Table IV. $[Et_2AlOLi]\cdot[Me_2AlOiPr]$ was prepared by complexation of Et_2AlOLi with $Me_2AlOiPr$, prepared by equimolar reaction of $AlMe_3$ with *i*-PrOH and purified by distillation under a reduced pressure, bp 60° (1 mm), at 60° in toluene for 3 hr. Completion of the complexation was confirmed by nmr spectroscopy where disappearance of broad resonances due to Et_2AlOLi was observed.

Reaction of Acetaldehyde with Organoaluminum Compounds.—A cylindrical two-necked reactor attached to a vacuum line was filled by dry argon. Transfer of reagents was made by the aid of an argon-flushed hypodermic syringe. In a typical procedure, 0.13 ml of acetaldehyde chilled at −78° was added to a solution of 4.7×10^{-4} mol of $[Et_2AlOLi]\cdot[AlEt_3]$ in 5 ml of toluene which was kept at −20°, with stirring magnetically from the outside of the reactor. The reactor was sealed and stirring was continued at −20°. After 24 hr, the reactor was opened at −78° to add 1 ml of 2 *N* sulfuric acid. The aqueous portion froze immediately. The mixture was gradually (in 10 min) warmed up to room temperature, with stirring. The icy portion melted as the hydrolysis started. After cooling to −78° again, the mixture was neutralized with 2 *N* NaOH solution by gradual elevation of the temperature. The mixture was cooled to −78° with stirring to solidify the aqueous portion. Unsolidified toluene layer was subjected to glc analysis. (During the hydrolysis treatments, the neck of the reactor was chilled by Dry Ice to avoid elimination of volatile materials.)

Gas Chromatographic Analysis.—A Yanagimoto gas chromatograph GCG-220 apparatus was operated at 70° using a 2-m 15% tricresyl phosphate/Celite-545 (50–60 mesh) column, with eluting by hydrogen gas at a flow rate of 40 ml/min. Quantitative analysis was carried out by calibration with known amounts of corresponding authentic samples in 5 ml of toluene. Toluene was used as an internal standard. Accuracy of the analyses is ±5% except for ethanol (±10%, mainly due to high solubility in water) and acetaldehyde (±15%, due to solubility in water plus vaporization).

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[30] N. Davidson and H. C. Brown, *J. Amer. Chem. Soc.*, **64**, 316 (1942); E. G. Hoffmann, *Justus Liebigs Ann. Chem.*, **629**, 104 (1960).

TABLE VI

$AlR_3 \cdot Do$ COMPOUNDS PREPARED

$AlR_3 \cdot Do$	Bp, °C (0.5 mm)	Calcd			Found			Nmr[a]			ΔH_f,[c] kcal/mol
		Al, %	Mol wt	R_3Al/Do	Al, %	Mol wt	R_3Al/Do[b]	δ_{CH_3C}	δ_{CH_2Al}	$\Delta\delta_{CH_2CH_3}$	
$Et_3Al \cdot OEt_2$	63–64	14.33	188.3	1.00	14.32	180.5	1.00	1.41	0.17	−1.24	11.2[d]
$Et_3Al \cdot THF$	62–63	14.49	186.3	1.00	14.35	183.2	0.97	1.44	0.20	−1.24	14.0[d]
$Et_3Al \cdot NEt_3$	77–78	12.53	215.4	1.00	12.58	214.8	0.99	1.53	0.25	−1.28	
$Et_3Al \cdot Py$	92–93	13.96	193.3	1.00	13.89	191.1	0.91	1.46	0.37	−1.09	19.4[d]
$Me_3Al \cdot OEt_2$	22.5–23	18.45	146.2	1.00	17.45	146.6	1.00		−0.45[f]		20.2[e]
$Me_3Al \cdot THF$	31–32	18.71	144.2	1.00	17.56	148.0	1.00		−0.50[f]		22.9[e]
$Me_3Al \cdot NEt_3$	Mp 66	15.57	173.3	1.00	14.59	163.8	0.98		−0.41[f]		26.5[e]
$Me_3Al \cdot Py$	64–66	17.85	151.2	1.00	17.41	148.2	1.00		−0.29[f]		17.5[e]

[a] Chemical shift in benzene solution at 60 MHz. Values are internally standardized from benzene proton assumed as 7.37 ppm. [b] Determined from nmr spectra. [c] Heats of formation of complexes $AlR_3 \cdot Do$. [d] Reference 19. [e] Reference 20. [f] δ_{CH_3Al}.

Reaction of Acetaldehyde with R_2AlZM.—For Et_2AlOLi four runs were carried out with 3 molar equiv of acetaldehyde for 24 hr (at −78°, −20, and 0°) and with 100 molar equiv of acetaldehyde for 20 hr at 0°. Acetaldehyde was recovered almost unchanged. No detectable peaks were observed other than the solvent and the starting aldehyde. For Me_2AlOLi, three runs were made with 3 molar equiv of acetaldehyde for 20 hr at −78, −20, and 0°. The results were identical with the case of Et_2AlOLi. For $Et_2AlNPhLi$, two runs were made of reactions with 3 molar equiv of acetaldehyde for 20 hr at −78 and at −20°. The results were also identical with the case of Et_2AlOLi. For Et_2AlSNa, with 3 molar equiv of acetaldehyde, the reaction for 24 hr at −78° was identical with the case of Et_2AlOLi. At −20°, 0.14 molar equiv of ethyl acetate was observed as a sole reaction product. With 100 molar equiv of the aldehyde, 1.08 molar equiv of ethyl acetate accompanied by trace amounts of ethanol, methyl ethyl ketone, and *sec*-butyl acetate was detected after 24 hr at −20°.

Registry No.—Acetaldehyde, 75-07-0.

Acknowledgment.—We are grateful to Messrs. N. Oguni and M. Mikumo for preparation of some organoaluminum complexes.

A Mechanistic Study of the Reaction of Lithium Aluminum Hydride with *N*-Methylbenzanilides

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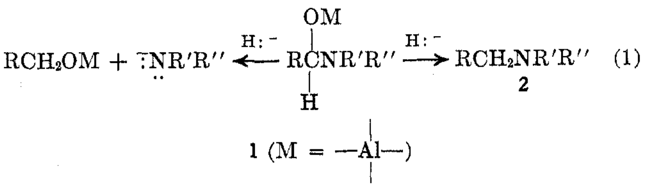
Received August 18, 1972

The relative rates of reduction *vs.* cleavage for various *N*-methylbenzanilides under the influence of lithium aluminum hydride are strongly dependent on the nature of substituents in the *N*-phenyl group. The effect of substituents in the *C*-phenyl moiety is small. The mechanistic implications of these observations are discussed. Investigations directed towards using *N*-methyl-*p*-chloroanilides for the preparation of aldehydes and the use of $LiAlH_4$–$AlCl_3$ for the reduction of *N*-methylbenzanilide are also described.

The reduction of tertiary carboxamides with lithium aluminum hydride normally results in the formation of the corresponding amine.[1] In a significant number of cases, however, reductive cleavage (hereafter referred to simply as cleavage) of the peptide bond occurs to yield an aldehyde and/or an alcohol, as well as the amine derived from the cleavage process.[1–7] In spite of the great utility of both types of reactions in the synthesis of amines and aldehydes, no systematic study of electronic factors and their influence on the relative importance of reduction *vs.* cleavage has been conducted. Accordingly, we have conducted such a study in hopes of increasing the mechanistic understanding and synthetic utility of these reactions.

Both the reduction and cleavage of tertiary carboxamides are commonly believed to result from partitioning of an initially formed tetrahedral adduct (**1**).[1–4] Aldehyde has been proposed to result from hydrolysis of **1**, while the other products arise from nucleophilic attack by hydride on **1** (eq 1).[2] An alternate proposal[8] suggests that expulsion of amide ion from **1** yields aldehyde,[9] while formation and subsequent reduction of **3** is responsible for the "normal" reduction process to yield **2** (eq 2).



$$RCH_2OM + {}^{-}\ddot{N}R'R'' \xleftarrow{H:^-} R\underset{H}{\overset{OM}{C}}NR'R'' \xrightarrow{H:^-} \underset{\mathbf{2}}{RCH_2NR'R''} \quad (1)$$

$$\mathbf{1}\ (M = -Al-)$$

$$RCHO + {}^{-}\ddot{N}R'R'' \longleftarrow \mathbf{1} \longrightarrow \underset{\mathbf{3}}{RCH{=}\overset{+}{N}R'R''} \xrightarrow{H:^-} \mathbf{2} \quad (2)$$

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(1) N. G. Gaylord, "Reduction with Complex Metal Hydrides," Interscience, New York, N. Y., 1956, Chapter 10.

(2) H. C. Brown and A. Tsukamoto, *J. Amer. Chem. Soc.*, **83**, 4549 (1961).

(3) W. Weygand, E. Eberhardt, H. Linden, F. Schofer, and I. Eigen, *Angew. Chem.*, **65**, 525 (1953).

(4) V. M. Micovic and M. L. Mihailovic, *J. Org. Chem.*, **18**, 1190 (1953). These authors suggest different intermediates for reduction and cleavage. They subsequently propose a single intermediate for both processes; see V. M. Micovic and M. L. Mihailovic, "Lithium Aluminum Hydride in Organic Synthesis," Izdavacko Preduzece, Belgrade, Yugoslavia, 1955, pp 58–60.

(5) F. Weygand and R. Mitgau, *Chem. Ber.*, **88**, 301 (1955).

(6) H. C. Brown and A. Tsukamoto, *J. Amer. Chem. Soc.*, **81**, 502 (1959).

(7) T. Axenrod, L. Loew, and P. S. Pregosin, *J. Org. Chem.*, **33**, 1274 (1968).

(8) Reference 1, p 545.

(9) Further reduction by $LiAlH_4$ would, of course, produce the corresponding alcohol.