Contribution from the Department of Polymer Science,
Faculty of Science, Osaka University, Toyonaka, Osaka, Japan 560

Synthesis of Binuclear Organoaluminum Compounds Containing Oxygen, Nitrogen, and Sulfur Atoms[1]

TAKANOBU AOYAGI, TAKEO ARAKI,* NOBUKI OGUNI, MASATOSHI MIKUMO, and HISAYA TANI

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Compounds of the type $[R_2AlZM][AlR_3]$ (where M = alkali metal; Z = O, NR′, or S; R and R′ = alkyl groups) have been prepared by the reaction of trialkylaluminum compounds in a molar ratio of 2:1 with alkali metal hydroxides (for $Z = O$), lithium N-substituted amides (for Z = NR′), and sodium hydrosulfide (for Z = S). In most cases the complexes were isolated in crystalline form. The reaction was shown to involve two stages, *viz*., $AlR_3 + MZH \rightarrow R_2AlZM + RH$, followed by $R_2AlZM + AlR_3 \rightleftharpoons [R_2AlZM][AlR_3]$, since the intermediate products R_2AlZM have also been isolated and shown to react with AlR_3 to give the complex. The latter is considered to be a binuclear donor-acceptor complex, in which R_2AlZM acts as an electron donor and AlR_3 as an acceptor. Infrared spectra of the oxygen-containing complexes $[Et_2AlOM]$-$[AlEt_3]$ where M = Li, Na, K, or Cs show that they have closely similar structures.

In a previous paper[2] we reported the discovery of new catalyst systems for the polymerization of acetaldehyde giving highly isotactic polyacetals with desirable film-forming properties. The catalysts are formed by allowing a trialkylaluminum compound to react with an alkali metal hydroxide in a molar ratio 2:1, and preliminary studies showed that in most cases the product of this reaction could be isolated in crystalline form. The only previous mention of this type of reaction is a brief statement by Ziegler[3] that triethylaluminum reacts with sodium hydroxide to give $Na[Et_2AlOAlEt_3]$. In view of the importance of these compounds as stereoregulating catalysts for polymerization reactions, we have made a general study of their formation and properties and have found that the same type of reaction occurs with a wide variety of alkyl substituents, alkali metals, and heteroatoms. The results enable us to make some generalizations concerning the nature of the reaction and the chemical constitution of the products.

Results and Discussion

Trialkylaluminum compounds (AlR_3 where R = methyl, ethyl, or isobutyl) undergo very facile reactions with alkali metal hydroxides (MOH where M = Li, Na, K, or Cs) to form pentaalkyldialuminum compounds (R_5Al_2OM) when the molar ratio AlR_3:MOH is 2:1. In the course of this reaction the corresponding alkane RH is evolved in a quantity equivalent to the amount of metal hydroxide present. When the metal hydroxide is replaced by an N-substituted lithioamide (R′NHLi where R′ = phenyl, benzyl, or *n*-butyl) or by sodium hydrosulfide, the analogous nitrogen- and sulfur-containing compounds are formed.

$$\begin{aligned} &2AlR_3 + MOH \rightarrow R_5Al_2OM + RH \\ &2AlR_3 + R'NHLi \rightarrow R_5Al_2NR'Li + RH \qquad (1) \\ &2AlR_3 + NaSH \rightarrow R_5Al_2SNa + RH \end{aligned}$$

In the preparation of the sulfur analog, a minor difficulty was encountered due to its dissociation in dilute solution, giving R_2AlSNa as the main product. This was overcome by mixing the reagents in concentrated solution. The ease with which the products could be crystallized varied considerably. Most of the compounds, though not all, were obtained in crystalline form, and the various methods used in the individual cases are described in the Experimental Section.

Analysis of the products confirmed that all had the general stoichiometric formula R_5Al_2ZM (where Z = O, NR′, or S) identical with that reported by Ziegler[3] for the product of the reaction between $AlEt_3$ and NaOH. A cryoscopic determination of the molecular weights of four of the products in benzene solution showed that Et_5Al_2OLi (I), $(i\text{-Bu})_5Al_2OLi$ (VI), and Et_5Al_2NPhLi (XII) were monomeric at all concentrations, while Et_5Al_2ONa (II) was monomeric only at high dilution.

The two-step nature of the reaction was demonstrated by the isolation, in five instances, of an intermediate R_2AlZM which reacted with an equimolar quantity of the trialkylaluminum to give R_5Al_2ZM. (The five intermediates isolated were Et_2AlOLi (XVIII), Et_2AlONa (XXI), Me_2AlOLi (XX), $Et_2AlNPhLi$ (XXII), and Et_2AlSNa (XXVI)). Thus the overall reaction in a hydrocarbon medium is envisaged as

$$AlR_3 + MZH \xrightarrow[a]{-RH} R_2AlZM \underset{b}{\overset{+AlR_3}{\rightleftharpoons}} [R_2AlZM][AlR_3] \qquad (2)$$

The first stage a involves the reaction of AlR_3 (presumably monomeric) with MZH to give R_2AlZM with evolution of alkane. The choice of monomeric rather than dimeric trialkylaluminum as the reacting species is based on the experimental observation that the reactivity of AlR_3 is in the order $Al(i\text{-Bu})_3 > AlEt_3 > AlMe_3$, *i.e.*, in line with their expected degree of dissociation in solution. Thus $Al(i\text{-Bu})_3$ is largely monomeric in dilute solution[4] ($\Delta H_D[(Al(i\text{-Bu})_3)_2(l)] = -8.1$ kcal mol^{-1}; *cf.* $\Delta H_D[(AlEt_3)_2(l)] = -16.9$ kcal mol^{-1}),[4a] and though $AlEt_3$ and $AlMe_3$ are partly associated to dimers in solution, the heats of formation of the dimers in the gaseous state ($\Delta H_f°(g) = -19.5 \pm 5$ and -21 ± 2 kcal mol^{-1} for $AlEt_3$ and $AlMe_3$, respectively[5]) indicate that $AlEt_3$ is less associated than $AlMe_3$. The alkali metal hydroxides, on the other hand, were reactive in the reverse order of their basic dissociation constants, suggesting that the first stage a of the reaction involves the electrophilic addition of AlR_3 to solid MOH, followed by proton abstraction from MOH by the alkyl anion R^-.

The preparation of the intermediate R_2AlZM compounds by the reaction of equimolar amounts of AlR_3 and MZH is

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[1] The investigation of compounds containing oxygen forms part of the Ph.D. thesis of Dr. T. Aoyagi, Osaka University, 1967.

[2] (a) H. Tani, T. Aoyagi and T. Araki, *J. Polym. Sci., Part B*, 2, 921 (1964); (b) T. Aoyagi, T. Araki, and H. Tani, *J. Polym. Sci., Part A-1*, 10, 2523 (1972).

[3] K. Ziegler in "Organometallic Chemistry," Reinhold, New York, N. Y., 1960, p 206.

[4] (a) M. B. Smith, *J. Organometal. Chem.*, 22, 273 (1970); *cf.* (b) K. Ziegler, W. R. Kroll, W. Larbig and O. W. Steudel, *Justus Liebigs Ann. Chem.*, 629, 53 (1960); (c) K. Ziegler, H. G. Gellert, E. Holzkamp, M. Soll, and W. R. Kroll, *ibid.*, 629, 172 (1960); (d) H. G. Hoffmann, *ibid.*, 629, 104 (1960).

[5] H. A. Skinner, *Advan. Organometal. Chem.*, 2, 72 (1964).

complicated by the fact that AlR_3 reacts more rapidly with R_2AlZM in stage b than it did with MZH in stage a. Thus the production of some R_5Al_2ZM could not be avoided but was minimized by keeping the concentration of AlR_3 low and followed by fractional crystallization to separate R_2AlZM from R_5Al_2ZM. Moreover, formation of R_2AlZM due to protolysis of R_5Al_2ZM by MZH was almost impossible as this reaction was extremely slow. (An alternative method of preparing R_2AlONa containing higher alkyl groups from R_2AlH and NaOH has been reported[6] but was found to be unsuitable for the lower alkyl derivatives, because unreacted R_2AlH cannot easily be separated from the product.) The separation of R_2AlZM from R_5Al_2ZM by fractional crystallization from a suitable solvent was repeated until the Grignard addition test[7,8] showed that no R_5Al_2ZM remained.

Et_2AlOLi (XVIII) obtained in this way was found to be soluble in benzene with an average degree of association corresponding to that of a hexamer. The degree of association appeared to be variable, since its solubility decreased on storage or heating.

Me_2AlOLi was obtained as a monoetherate (XIX) from the equimolar reaction of $AlMe_3$ with LiOH in the presence of an ether, *e.g.*, diethyl ether, tetrahydrofuran, or anisole. The etherates were soluble in ethers and aromatic hydrocarbons and readily decomposed in boiling toluene to precipitate ether-free Me_2AlOLi (XX), which was insoluble in aromatic hydrocarbons.

The effectiveness of the ethers in promoting reaction between $AlMe_3$ and LiOH was in the order anisole > diethyl ether > tetrahydrofuran. This is in accord with our suggestion that the reactive species may be monomeric $AlMe_3$, since in the presence of an ether its concentration will be governed by the dissociation equilibrium

$$Me_3Al{\cdot}OR_2 \rightleftharpoons Me_3Al + R_2O$$

and the promoting effect of an ether should therefore be an inverse function of its donor strength. Anisole is a much weaker donor than tetrahydrofuran, as shown by their heats of addition to $AlEt_3$ (2-3 kcal mol^{-1} for anisole and 14 kcal mol^{-1} for tetrahydrofuran[9]), while diethyl ether (11 kcal mol^{-1})[9] has an intermediate donor strength closer to that of tetrahydrofuran.[10] This order of donor strength was in accord with the observed ease of removal of the ethers from the Me_2AlOLi–ether complexes, governed by the equilibrium

$$Me_2AlOLi{\cdot}OR_2 \rightleftharpoons Me_2AlOLi + R_2O$$

The compound $Et_2AlNPhLi$ (XXII) was obtained as a solid which was largely insoluble in aromatic hydrocarbons, although extraction with toluene gave a solution from which a small amount of a crystalline trimer was isolated, indicating that the bulk of the insoluble product consisted of tetramer or higher polymers. The analogous sulfur-containing intermediate Et_2AlSNa (XXVI) was also obtained as a white powder insoluble in aromatic hydrocarbons.

Having isolated some of the intermediate R_2AlZM compounds, it was possible to perform stage b of reaction 2 as a separate reaction. $AlEt_3$ was allowed to react in an equimolar quantity with Et_2AlOLi, Et_2AlONa, and $Et_2AlNPhLi$, respectively, in toluene solution and gave crystalline complexes without any gas evolution. Analyses of these complexes, combined with mixture melting point determination and nmr spectroscopy,[11] showed that they were identical with the corresponding products obtained from the overall reaction 1. In two cases ($[Et_2AlOLi][AlEt_3]$ and $[Et_2AlONa][AlEt_3]$) further confirmation was obtained by infrared spectroscopy. Two of the intermediates, Me_2AlOLi and Et_2AlSNa, were polymeric and insoluble in toluene, and stage b was performed in suspension rather than in solution. Thus when $AlMe_3$ was added to a suspension of Me_2AlOLi in toluene, the Me_2AlOLi dissolved and the complex $[Me_2AlOLi][AlMe_3]$ subsequently precipitated. Similar behavior was observed in the addition of $AlEt_3$ to Et_2AlSNa, although here it was necessary to use high concentrations to obtain $[Et_2AlSNa][AlEt_3]$ which readily dissociates in dilute solution (or on washing, heating, or storage). Although stage b is an equilibrium process, this dissociation is important only for the sulfur compound and virtually negligible for the oxygen and nitrogen derivatives, where the coordinate bond to aluminum is much less labile than that of sulfur.[9,12,13] For the oxygen and nitrogen derivatives, therefore, the slower stage a of reaction 2 would be the rate-determining process.

The demonstration that stage b of reaction 2 can be isolated as a separate process opens up the possibility of adding an alternative trialkylaluminum to R_2AlZM to form $[R_2AlZM][AlR'_3]$, in which two different kinds of alkyl group are incorporated in a 2:3 molar ratio. The following examples of mixed-alkyl complexes have been prepared: $[Et_2AlOLi][AlMe_3]$ (VIII), $[Et_2AlOLi][Al(i\text{-}Bu)_3]$ (IX), $[Me_2AlOLi][AlEt_3]$ (X), $[Et_2AlONa][AlMe_3]$ (XI), $[Et_2AlNPhLi][AlMe_3]$ (XVII), $[Et_2AlNPhLi][Al(i\text{-}Bu)_3]$ (XXIII), and $[Et_2AlSNa][AlMe_3]$ (XXV). There does not appear to be any intramolecular exchange of alkyl groups in solution, even in the presence of excess AlR'_3; *e.g.*, for the $[Et_2AlOLi][AlMe_3]$ complex, analysis showed that the ratio of ethyl to methyl groups was consistently 2:3, independent of the molar ratio of Et_2AlOLi to $AlMe_3$ in the reaction mixture. Preliminary investigation has shown that mixed complexes of this type can also be formed with Lewis acids other than AlR'_3, *e.g.*, Et_2AlH, $ZnEt_2$, and $MgEt_2$.

Finally, we have examined the infrared spectra in benzene or toluene solution of the complexes formed from $AlEt_3$ and the alkali metal hydroxides (I, II, III, IV) as well as those of $[(i\text{-}Bu)_2AlOLi][Al(i\text{-}Bu)_3]$ and the intermediate Et_2AlOLi. The absorption bands are given in Table I, together with those of Et_6Al_2 and $(i\text{-}Bu)_3Al$ (in cyclohexane solution[14]), and tentative assignments are indicated.

Absorptions due to Al-R groups are clearly identifiable from the corresponding absorptions for AlR_3.[14] Bands appearing in the region 690-775 cm^{-1} are ascribed to Al-O-Al symmetric stretching ($\nu_{1(AlOAl)}$), which occurs at ~700 cm^{-1} in aluminum suboxide Al_2O.[15] (Strong absorptions in the range 690-770 cm^{-1} are also observed for $R_2AlOAlR_2$.[16,17]) Bands at 800-900 cm^{-1} are assigned to Al-O-M symmetric

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[6] French Patent 879,005 (1961).

[7] This involves the addition of acetaldehyde in toluene solution at 0°. In the presence of either AlR_3 or $[R_2AlZM][AlR_3]$ reaction occurs to give *sec*-butyl alcohol after hydrolysis. This test has been shown[8] to be very sensitive in detecting small amounts of $[R_2AlZM][AlR_3]$ in R_2AlZM.

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[9] E. Bonitz, *Chem. Ber.*, **88**, 742 (1955).

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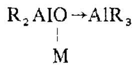
Table I. Infrared Spectra of Organoaluminum Compounds

Et_5Al_2OLi[a] I	Et_5Al_2ONa[a] II	Et_5Al_2OK[a] III	Et_5Al_2OCs[a] IV	Et_6Al_2 [b]	Et_2AlOLi[c] XVIII	$(i\text{-}Bu)_5\text{-}Al_2OLi$[c] VI	$(i\text{-}Bu)_3Al$[b]	Assignment[b]
2940 m	2940 m	2955 m	2960 m		2940 m	2950 w		ν(CH)
2895 sh	2900 w	2910 w	2880 w		2895 sh	2895 sh		
2860 s	2860 s	2880 s	2840 s		2860 s	2855 s		
2790 m	2790 m	2805 m	2795 m		2785 m	2770 m		
2720 w	2720 w	2720 w	2720 w		2720 w	2615 w		
1463 sh	1465 sh	1470 sh	1460 sh	1470 s	1463 sh	1465 s	1465 s	$\delta_{as}(CH_3)$
1455 m	1455 m	1460 m	1455 m	1458 sh	1455 m	1455 sh	1455 sh	
1407 s	1410 s	1412 s	1410 s	1412 m	1410 s	1405 m	1396 m	$\delta(CH_2Al)$
1395 sh	1387 sh	1395 sh	1385 sh	1401 sh		1388 sh		$\delta(CH_2Al)_{Br}$
1385 sh		1390 sh		1389 sh				
1370 w	1373 w	1375 w	1370 w	1379 sh	1378 w	1378 m	1380 m	$\delta_s(CH_3)$
						1363 s	1362 s	
1257 w	1258 w	1263 w	1258 w		1264 w			
1226 m	1227 m	1230 m	1224 m	1230 m	1227 m	1205 w	1198 sh	$\gamma, \tau(CH_2Al)$
1190 sh	1192 s	1185 s	1178 s	1199 m	1193 s	1186 sh	1182 sh	
1182 s					1185 sh	1175 s	1173 s	
						1163 sh	1158 sh	
						1316 m	1320 m	$\gamma, \tau(CH_2)$
1152 w	1160 w	1155 w	1150 sh		1153 w	1138 w		
	1153 w							
1112 m	1102 m	1108 m	1112 m		1103 sh	1108 w		$\nu_3(AlOM), \nu_3(AlOAl)$
1080 m	1065 m	1080 m	1067 m		1073 sh	1050 sh		
1045 w	1037 w	1068 w			1057 m	1030 m		
1026 w		1045 w			1033 sh			
		1028 w						
						1064 s	1064 s	
						1015 m	1010 m	
985 s	988 s	993 s	988 s	985 s	985 s	960 sh	953 sh	ν(CC)
						945 m	943 w	
948 m	954 m	952 m	944 m	955 m	955 m	850 sh	812 m	ν_s(CC)
917 m	918 w	920 m	916 m	921 m	922 m	815 m		
885 w	895 w	880 w	860 w		895 sh	916 w		$\nu_1(AlOM)$
	872 w							
825 ~800 w, br	825 ~800 w, br	823 ~795 w, br	808 sh, br	835 sh 805 s				
772 m	772 sh	765 m	750 sh		755 sh	765 s		$\nu_1(AlOAl)$
730 sh	745 m	717 sh	737 s		730 sh			
	730 sh							
700 s	710 ~690 s	707 s	708 sh		700 w	735 s		
645 s	640 s	650 s		662 m	630 s	670 s	685 m	ν_8 ν_{11} ν_{as}
			625 s					
618 sh	618 sh	626 sh		626 m		640 sh	655 sh	ρ (α C)
515 w	520 sh	500 sh	525 sh	533 w	530 s	570 sh	545? vw	$\nu_1(\nu_s)$
			495 sh			522 w	490? vw	
						470 m	430? vw	
						430 m		
475 w	492 w	?	468 w	477 w	475 sh			$\nu_{13}(\nu_{Br})$
				470 sh	460 w			

[a] In benzene. [b] Cited from ref 14, in cyclohexane. [c] In toluene.

stretching ($\nu_{1(AlOM)}$), since they were much stronger in Et_2AlOLi than in $[R_2AlOM][AlR_3]$. Some support for this assignment may be derived from Mann and Linevsky's[18] observation of the $\nu_{1(LiOLi)}$ frequency in Li_2O at ~760 cm^{-1}. The absorptions tabulated between 1010 and 1110 cm^{-1} were relatively weak and are tentatively assigned to bent asymmetric stretching (ν_3) of Al-O-Al coupled with Al-O-M groupings. Frequencies observed in this region are close to those of $\nu_{3(AlOAl)}$ in Al_2O (at 950 cm^{-1}),[15] $\nu_{3(AlOAl)}$ in $Al(OR)_3$ (at 900-1000 cm^{-1}),[19-21] and $\nu_{3(LiOLi)}$ in Li_2O (at 990 cm^{-1}).[18]

Although detailed assignments of absorption frequencies are only tentative, it is clear that all of the R_5Al_2OM complexes studied have closely similar spectra which do not conflict with the structure, *viz.*[22]



$$\underset{\displaystyle M}{\underset{|}{R_2AlO}}\rightarrow AlR_3$$

where R_2AlOM acts as a Lewis base and AlR_3 as a Lewis acid. Further details of nmr study on the structure of this series of compound will be seen in a separate paper.[11]

Experimental Section

In view of the high reactivity of the organoaluminum compounds

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(18) D. E. Mann and M. J. Linevsky, *J. Chem. Phys.*, **39**, 2463 (1963).

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(20) R. C. Wilhoit, J. R. Burton, F.-T. Kuo, S.-R. Huang, and A. Vignesnel, *J. Inorg. Nucl. Chem.*, **24**, 851 (1962).

(21) F. A. Scott, J. Goldenson, S. E. Wiberley, and W. H. Bauer, *J. Phys. Chem.*, **58**, 61 (1954).

(22) An attempt to measure the conductivity of $[Et_2AlOLi]$-$[AlEt_3]$ was unsuccessful, as the conductivity was below the limit of the apparatus available. However, the fact that the conductivity was so low indicates that the nonionic structure suggested is reasonable.

with atmospheric oxygen and moisture, all of the experiments described, including solvent purification, molecular weight determinations, and measurements of infrared and nmr spectra, were performed in an atmosphere of argon.

Materials. Hexane, decalin, toluene, *m*-xylene, diethyl ether, anisole, and tetrahydrofuran were purified and dried by standard methods, followed by drying over CaH_2 and distillation. $AlMe_3$, $AlEt_3$, and $Al(i\text{-}Bu)_3$ (Ethyl Corp.) were used after a single distillation *in vacuo*. Aniline, *n*-butylamine, and benzylamine were distilled, dried with lithium metal, and then redistilled. Alkali metal hydroxides were dried over P_2O_5 *in vacuo* (*e.g.*, LiOH was dried *in vacuo* at 140° for 24 hr with P_2O_5[23]). *n*-Butyllithium, supplied commercially as a solution in heptane, was used without further purification. Sodium hydrosulfide was prepared as a white powder from sodium ethoxide and hydrogen sulfide in ethanol.[24] It was shown to be free of ethoxy groups by glc examination of the ether extract after treating with water.

Analysis. Aluminum was analyzed gravimetrically using the 8-hydroxyquinoline method. The evolution of gas was monitored by volumetric gasometry, and the gases were analyzed by glc. (For methane and ethane a 2-m silica gel column at 50° was used, and for isobutane a 2-m β,β'-oxydipropionitrile–silica gel column[25] at 50°.) Molecular weights were determined cryoscopically in benzene solution at at least three different concentrations.

Preparation of Organoaluminum Compounds. (i) Pentaethyldialuminum Lithiooxide, $[Et_2AlOLi][AlEt_3]$ (Ia). One-Step Method. To a suspension of anhydrous LiOH (1.2 g, 0.05 mol) in toluene (40 ml), a slight excess of $AlEt_3$ (13.9 ml, 0.102 mol) was added dropwise, giving nearly quantitative evolution of ethane (~0.05 mol) at 70°. The reaction was completed at 70°, and a small amount of unreacted LiOH was filtered. Cooling the filtrate to 20° gave colorless needle crystals (*ca.* 80% yield), mp 142°, after recrystallization from toluene. *Anal.* Calcd for $C_{10}H_{25}OLiAl_2$: Al, 24.3; Et:Al ratio, 2.5; mol wt 222. Found: Al, 23.5; Et:Al ratio, 2.2; mol wt 229.

(ii) Pentaethyldialuminum Lithiooxide (Ib). Two-Step Method. (a) Preparation of Lithium Diethylaluminate, Et_2AlOLi (XVIII). To a suspension of LiOH (2.4 g, 0.10 mol) in *m*-xylene (40 ml) heated to *ca.* 80°, a slightly less than equimolar quantity of $AlEt_3$ (13.4 ml, 0.098 mol) was slowly added dropwise to maintain a vigorous evolution of ethane. The reaction was completed under reflux and filtered. The filtrate was concentrated under reduced pressure, and *n*-hexane was then added to precipitate the by-product I. (This process was repeated several times to ensure complete removal of I.) On evaporation of the filtrate at 10–20 mm pressure, a white caramellike solid was obtained; yield *ca.* 60%; mp >200°. *Anal.* Calcd for $C_4H_{10}OLiAl$: Al, 25.0; Et:Al ratio, 2.0; mol wt 108. Found: Al, 23.2; Et:Al ratio, 1.8; mol wt 663 (average hexamer). Nmr: δ 1.46 (broad singlet, 3.02 protons, CH_3), 0.12 (broad singlet, 2.00 protons, CH_2–Al) using benzene as internal reference (assumed 7.37 ppm). The compound became insoluble in aliphatic hydrocarbons after storage for about 10 days, or alternatively on heating. The insoluble material gave analysis figures identical with those of XVIII above, apart from the molecular weight. XVIII did not form an ethyl-addition product (*sec*-butyl alcohol) on treatment with acetaldehyde at 0°.

(b) Formation of Complex from XVIII and $AlEt_3$. To a solution of XVIII (1.08 g, 0.01 mol) in 5 ml of toluene, a solution of $AlEt_3$ (1.37 ml, 0.01 mol) in 5 ml of toluene was added dropwise under stirring at −40°.[26] During the reaction a crystalline product precipitated rapidly without evolution of gases. After filtration followed by recrystallization from toluene solution, a nearly quantitative yield of colorless needle crystals was obtained which was identified with Ia by mixture melting point measurement. *Anal.* Calcd: see part i. Found: Al, 23.8; Et:Al ratio, 2.3; mol wt 225.

(iii) Pentaethyldialuminum Sodiooxide, $[Et_2AlONa][AlEt_3]$ (II). Reaction and procedure were as described in part i, using NaOH (2.0 g, 0.05 mol) with $AlEt_3$ (13.9 ml, 0.102 mol) in 40 ml of toluene. Filtration followed by evaporation of the reaction mixture gave a white crystalline residue which was then washed with *n*-hexane at −78° and recrystallized from an *n*-hexane–benzene mixture (2:1 v/v) to give *ca.* 80% yield of colorless needle or prismatic crystals, mp 165°. *Anal.* Calcd for $C_{10}H_{25}ONaAl_2$: Al, 22.7; Et:Al ratio, 2.5; mol wt 238. Found. Al, 23.2; Et:Al ratio, 2.56; mol wt 245 (at 0.015 g/ml) and 469 ± 6 (at 0.038–0.061 g/ml).

(iv) Pentaethyldialuminum Potassiooxide, $[Et_2AlOK][AlEt_3]$ (III). Reaction and procedure were as in part i, using anhydrous KOH (2.8 g, 0.05 mol) with $AlEt_3$ (13.9 ml, 0.102 mol) in 40 ml of benzene. After filtering the reaction mixture, the filtrate was concentrated *in vacuo*. On standing at room temperature colorless prismatic crystals were formed from the filtrate, which were recrystallized from a concentrated benzene solution to give 50–60% yield of III, mp 173°. *Anal.* Calcd for $C_{10}H_{25}OKAl_2$: Al, 21.3; Et:Al ratio, 2.5. Found: Al, 20.5; Et:Al ratio, 2.4.

(v) Pentaethyldialuminum Cesiooxide, $[Et_2AlOCs][AlEt_3]$ (IV). Reaction and procedure were as in part i, using anhydrous CsOH (7.5 g, 0.05 mol) with $AlEt_3$ (13.9 ml, 0.102 mol) in 40 ml of benzene. The reaction mixture separated into two layers on standing. After the upper benzene layer was separated out, the lower viscous layer was throughly mixed with *n*-hexane, and the resultant mixture was allowed to stand to give two layers. Crystals grown at the surface of the lower viscous layer beneath the hexane layer were filtered and then washed with chilled hexane. The yield of the viscous oily product was *ca.* 90%, *ca.* 20% of which was obtained as colorless prismatic crystals, mp 126.5°. *Anal.* Calcd for $C_{10}H_{25}OCsAl_2$: Al, 15.5; Et:Al ratio, 2.5. Found: Al, 14.9; Et:Al ratio, 2.4.

(vi) Pentamethyldialuminum Lithiooxide, $[Me_2AlOLi][AlMe_3]$ (Va). One-Step Method. $AlMe_3$ (9.8 ml, 0.102 mol) and LiOH (1.2 g, 0.05 mol) were allowed to react in 32 ml of toluene containing 8 ml of diethyl ether, to form the soluble monoetherate of Va which was then recrystallized from toluene. The etherate was dissolved in boiling xylene and the ether was stripped off by elution with a stream of argon, which precipitated Va as a white powder. This was sublimed in a stream of hot decalin to give crystalline Va as colorless prisms, mp >200°. *Anal.* Calcd for $C_5H_{15}OLiAl_2$: Al, 35.5; Me:Al ratio, 2.5. Found: Al, 35.2; Me:Al ratio, 2.4. Va was insoluble in hydrocarbons but soluble in etheric solvents due to complex formation.

(vii) Pentamethyldialuminum Lithiooxide (Vb). Two-Step Method. (a) Preparation of Etherates of Lithium Dimethylaluminate, $[Me_2AlOLi][OR^1R^2]$ (XIX). Tetrahydrofuranate (XIXa, $R^1R^2 = -(CH_2)_4-$). The reaction was as described in part iia using $AlMe_3$ (14.4 ml, 0.15 mol), LiOH (4.8 g, 0.20 mol), and a toluene–THF mixture (8:2 v/v, 150 ml). When reaction was complete, the mixture was filtered at 50° and the filtrate was evaporated *in vacuo* to give a white powdery product. This was washed several times with *n*-hexane at 50° and then redissolved in excess toluene. The procedure of evaporation followed by washing and redissolution was repeated several times to give a yield of *ca.* 12 g. *Anal.* Calcd for $C_6H_{14}O_2LiAl$: Al, 17.8; Me:Al ratio, 2.0. Found: Al, 17.0; Me:Al ratio, 1.7. Hydrolysis followed by glc analysis gave THF in the quantity calculated for a mono(tetrahydrofuranate).

Diethyl Etherate (XIXb, $R^1 = R^2 = C_2H_5$). Procedure and quantities were as in part viia, but using a toluene–Et_2O mixture (8:2 v/v) gave a white powdery product; yield 11.5 g. Et_2O in a quantity corresponding to a monoetherate was detected by glc after hydrolysis.

Anisolate (XIXc, $R^1 = CH_3$, $R^2 = C_6H_5$. Procedure and quantities were as in part viia, but using 100 ml of anisole gave XIXc. Nmr (60 MHz in benzene): δ −0.47 (singlet, 1.99 protons, CH_3–Al), 3.73 (singlet, 1.0 proton, CH_3O) with external reference TMS at 0.00 ppm.

(b) Preparation of Ether-Free Lithium Dimethylaluminate, Me_2AlOLi (XX). From XIXa. A solution of XIXa (5 g) in 100 ml of boiling toluene was eluted with argon for 5 hr (*cf.* part vi) to remove THF. The white precipitate which gradually formed was collected, washed with toluene several times at room temperature, and then refluxed with toluene for 3 hr, after which the toluene and any residual THF were removed by evaporation *in vacuo*. This procedure was repeated three times, yield *ca.* 20%; mp >200°. *Anal.* Calcd for C_2H_6OLiAl: Al, 33.7; Me:Al ratio, 2.0. Found: Al, 33.1; Me:Al ratio, 1.8. The product, which was a white powder, contained only trace amounts of THF (detected by glc after hydrolysis) and was soluble in ethers, though only slightly soluble in toluene.

From XIXb and XIXc. Using the same procedure, XIXb gave a 40% yield and XIXc a 70% yield of a product which was identified as XX by analysis. Only trace amounts of residual anisole were detected either by nmr of a benzene solution (XX was slightly soluble in benzene) or by glc after hydrolysis.

(c) Formation of Complex from XX and $AlMe_3$, $[Me_2AlOLi]$-$[AlMe_3]$ (Vb) A procedure as in part iib gave a white powder which

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[26] A wide range of temperatures up to 100° can be applied for the complex formation.

was crystallized as described in part vi, to give an almost quantitative yield of colorless needle crystals, mp >200°. *Anal.* Calcd: see part vi. Found: Al, 35.2; Me:Al ratio, 2.4. Solubility behavior was identical with that of Va.

(viii) Pentaisobutyldialuminum Lithiooxide, [(*i*-Bu)$_2$AlOLi]-[Al(*i*-Bu)$_3$] (VI). Reaction and procedure were as described in part i using Al(*i*-Bu)$_3$ (12.7 ml, 0.0503 mol) and LiOH (0.6 g, 0.025 mol) in 40 ml of toluene. In this reaction, isobutane was evolved, and after filtering the reaction mixture, VI was deposited from the filtrate as colorless needle crystals, which were recrystallized from toluene; yield *ca.* 80%; mp 145°. *Anal.* Calcd for $C_{20}H_{45}OLiAl_2$: Al, 14.9; mol wt 362. Found: Al, 14.7; mol wt 367.

(ix) Pentaisobutyldialuminum Sodiooxide, [(*i*-Bu)$_2$AlONa]-[Al(*i*-Bu)$_3$] (VII). Reaction and procedure as described in part i using Al(*i*-Bu)$_3$ (12.7 ml, 0.0503 mol) and NaOH (1 g, 0.025 mol) in 40 ml of benzene. After filtration and evaporation, the product was recrystallized from hexane solution to give colorless prismatic crystals. The method of preparation was not consistently reliable, as the same procedure frequently gave (*i*-Bu)$_2$AlONa as a white powder, mp >200°. Nmr measurements showed that the stability of VII in benzene solution was slightly less than that of other complexes containing oxygen, but it was stable either in cyclohexane solution or in a cyclohexane–benzene mixture.[11]

(x) Diethyltrimethyldialuminum Lithiooxide, [Et$_2$AlOLi]-[AlMe$_3$] (VIII). The crystalline product obtained by treating XVIII (1.08 g, 0.01 mol) with AlMe$_3$ (0.96 ml, 0.01 mol) in toluene at room temperature (*cf.* part iib) was washed with toluene several times and recrystallized from toluene solution to give a nearly quantitative yield of colorless needle crystals, which melted in the range 104–143° (presumably double melting point). *Anal.* Calcd for $C_7H_{19}OLiAl_2$: Al, 30.0; (Et + Me):Al ratio, 2.5; Me:Et ratio, 1.50. Found: Al, 29.5; (Et + Me):Al ratio, 2.3; Me:Et ratio, 1.49. VIII was slightly soluble in aromatic hydrocarbons.

(xi) Diethyltriisobutyldialuminum Lithiooxide, [Et$_2$AlOLi]-[Al(*i*-Bu)$_3$] (IX). Reaction and procedure were as described in part iib, using XVIII (1.08 g, 0.01 mol) and Al(*i*-Bu)$_3$ (2.52 ml, 0.01 mol) in 5 ml of toluene. The product was recrystallized from toluene solution; yield *ca.* 90%; mp 70–76° (colorless needle crystals). *Anal.* Calcd for $C_{16}H_{37}OLiAl_2$: Al, 17.6. Found: Al, 17.4.

(xii) Dimethyltriethyldialuminum Lithiooxide, [Me$_2$AlOLi]-[AlEt$_3$] (X). The procedure was as in part iib using XX (0.80 g, 0.01 mol) and AlEt$_3$ (1.37 ml, 0.01 mol) in 5 ml of toluene, giving X as colorless needle crystals. The same product was obtained by complexing XX with AlEt$_3$ in molar ratios of either 2:1 or 1:2, the yield being nearly quantitative when based on the component present in smaller quantity. The product was purified by repeated washing with toluene; mp 98–143° (double-melting behavior, but less definite). *Anal.* Calcd for $C_8H_{21}OLiAl_2$: Al, 27.8; (Me + Et):Al ratio, 2.5; Et:Me ratio, 1.50. Found: Al, 27.0; (Me + Et):Al ratio, 2.3; Et:Me ratio, 1.47. Nmr (in toluene at room temperature): δ 0.69 (broad singlet, 6 protons, CH_3–C), −1.00 (broad singlet, 13.2 protons, CH_3–Al plus CH_2–Al) with external reference TMS at 0.00 ppm. X was slightly soluble in toluene.

(xiii) Diethyltrimethyldialuminum Sodiooxide, [Et$_2$AlONa]-[AlMe$_3$] (XI). (a) Sodium Diethylaluminate, Et$_2$AlONa (XXI). The procedure was as in part iia using AlEt$_3$ (13.9 ml, 0.102 mol) and NaOH (4.0 g, 0.10 mol) in ligroin (40 ml, bp 120–140°) to give XI as a white powder in *ca.* 50% yield; mp >200°. *Anal.* Calcd for $C_4H_{10}ONaAl$: Al, 21.8; Et:Al ratio, 2.0. Found: Al, 21.2; Et:Al ratio, 1.7.

(b) Formation of Complex from XXI and AlMe$_3$. The procedure was as in part iib using XXI (1.24 g, 0.01 mol) and AlMe$_3$ (0.96 ml, 0.01 mol) in 5 ml of hexane. The white powdery product was washed several times with *n*-hexane to give *ca.* 80% yield. *Anal.* Calcd for $C_7H_{19}ONaAl_2$: Al, 27.5; (Et + Me):Al ratio, 2.5; Me:Et ratio, 1.50. Found: Al, 27.0; (Et + Me):Al ratio, 2.3; Me:Et ratio, 1.43. Nmr (in toluene at room temperature): δ 0.75 (triplet, 6 protons, CH_3–C), −0.81 (quartet, 3.95 protons, CH_2–Al), −1.41, −1.45 and −1.49 (triple singlets, 8.5 protons, CH_3–Al).

(xiv) Pentaethyldialuminum Lithioanilide, [Et$_2$AlNPhLi]-[AlEt$_3$] (XIIa). One-Step Method. The procedure was as in part i, using PhNHLi (5.0 g, 0.051 mol, freshly prepared from aniline and *n*-BuLi) with AlEt$_3$ (13.9 ml, 0.102 mol) in 40 ml of toluene. The product was recrystallized from toluene solution to give *ca.* 80% yield of colorless needle crystals, mp 132°. *Anal.* Calcd for $C_{16}H_{30}NLiAl_2$: Al, 18.1; Et:Al ratio, 2.5; mol wt 297. Found: Al, 18.6; Et:Al ratio, 2.4; mol wt 293.

(xv) Pentaethyldialuminum Lithioanilide (XIIb). Two-Step Method. (a) Diethyl(*N*-lithioanilino)aluminum, Et$_2$AlNPhLi (XXIII). The procedure was as in part i, using PhNHLi (10.0 g, 0.101 mol) with AlEt$_3$ (13.4 ml, 0.098 mol) in 40 ml of toluene. On completion of the reaction, the hot mixture was filtered to remove unreacted PhNHLi, and on cooling the filtrate a solid was deposited (mainly XIIa). This was filtered out and the filtrate was heated again to give the desired product as an insoluble white powder (mp >200°) in *ca.* 60% yield. This was washed several times with toluene, and from the toluene extract a crystalline trimer was obtained (<10%) which was recrystallized from toluene to give colorless needle crystals, mp 110°. *Anal.* Calcd for $C_{10}H_{10}NLiAl$: Al, 14.7; Et:Al ratio, 2.0; mol wt 183. Found: Al, 15.8; Et:Al ratio, 1.9; mol wt 514. On refluxing the soluble trimer in toluene, it was converted into the insoluble form, which gave the same analysis figures apart from the molecular weight.

(b) Formation of Complex from XXII and AlEt$_3$. The procedure was as in part iib, using XXII (1.83 g, 0.01 mol) with AlEt$_3$ (1.37 ml, 0.01 mol) in 5 ml of toluene. The product was recrystallized from toluene solution to give *ca.* 85% yield of colorless needle crystals, mp 133°. *Anal.* Calcd: see part xiv. Found: Al, 17.7; Et:Al ratio, 2.3; mol wt 292. The product was identified as XIIa formed in part xiv by the mixture melting point method.

(xvi) Pentamethyldialuminum Lithioanilide, [Me$_2$AlNPhLi]-[AlMe$_3$] (XIII). The procedure was as in part xiv, using PhNHLi (5.0 g, 0.051 mol) with AlMe$_3$ (9.8 ml, 0.102 mol) in 40 ml of toluene. The reaction mixture was filtered at 50°, and on cooling the filtrate, tiny prismatic crystals were deposited, which were washed with toluene to give *ca.* 90% yield of crystalline XIII, mp >200°. *Anal.* Calcd for $C_{11}H_{20}NLiAl_2$: Al, 23.8. Found: Al, 23.7.

(xvii) Pentaisobutyldialuminum Lithioanilide, [(*i*-Bu)$_2$AlNPhLi]-[Al(*i*-Bu)$_3$] (XIV). The procedure was as in part xiv, using PhNHLi (5.0 g, 0.051 mol) with Al(*i*-Bu)$_3$ (25.4 ml, 0.106 mol) in 40 ml of toluene. The product was recrystallized from hexane solution to give *ca.* 70% yield of colorless needle crystals, mp 165°. *Anal.* Calcd for $C_{26}H_{50}NLiAl_2$: Al, 14.1. Found: Al, 14.5.

(xviii) Pentaethyldialuminum Lithiobenzylamide, [Et$_2$AlN-(CH$_2$Ph)Li][AlEt$_3$] (XV). The procedure was as in part xiv, using PhCH$_2$NHLi (5.6 g, 0.05 mol) with AlEt$_3$ (13.9 ml, 0.102 mol) in 40 ml of toluene. The product was recrystallized from toluene solution to give *ca.* 85% yield of colorless needle crystals, mp 153°. *Anal.* Calcd for $C_{17}H_{32}NLiAl_2$: Al, 17.3. Found: Al, 17.2.

(xix) Pentaethyldialuminum Lithio-*n*-butylamide, [Et$_2$AlN-*n*-BuLi][AlEt$_3$] (XVI). The procedure was as in part xiv, using *n*-BuLi (4.0 g, 0.051 mol) with AlEt$_3$ (13.9 ml, 0.102 mol) in 40 ml of toluene. The product was recrystallized from toluene to give *ca.* 75% yield of colorless needle crystals, mp 138°. *Anal.* Calcd for $C_{14}H_{34}NLiAl_2$: Al, 19.5. Found: Al, 19.7.

(xx) Diethyltrimethyldialuminum Lithioanilide, [Et$_2$AlNPhLi][AlMe$_3$] (XVII). The procedure was as in part iib, using XXII (1.83 g, 0.01 mol) with AlMe$_3$ (0.96 ml, 0.01 mol) in 5 ml of toluene. XXII dissolved immediately, followed by precipitation of the complex XVII, which was washed several times with toluene to give *ca.* 90% yield of powdery prismatic crystals, mp 185°. *Anal.* Calcd for $C_{13}H_{24}NLiAl_2$: Al, 21.1. Found: Al, 21.8.

(xxi) Diethyltriisobutyldialuminum Lithioanilide, [Et$_2$AlNPhLi]-[Al(*i*-Bu)$_3$] (XXIII). The procedure was as in part iib, using XXII (1.83 g, 0.01 mol) with Al(*i*-Bu)$_3$ (2.52 ml, 0.011 mol) in 5 ml of a toluene–Et$_2$O (9:1) mixture at room temperature. The product was repeatedly washed with *n*-hexane to remove the last traces of ether and was then recrystallized from toluene solution to give *ca.* 60% yield of colorless needle crystals. *Anal.* Calcd for $C_{22}H_{42}NLiAl_2$: Al, 14.1. Found: Al, 14.5.

(xxii) Pentaethyldialuminum Sodiosulfide, [Et$_2$AlSNa][AlEt$_3$] (XXIVa). Two-Step Method. (a) Sodium Diethylthioaluminate, Et$_2$AlSNa (XXVI). The reaction of freshly prepared white sodium hydrosulfide (1.4 g, 0.025 mol) with AlEt$_3$ (3.4 ml, 0.025 mol) in 40 ml of toluene gave *ca.* 85% yield of an insoluble white powdery product, mp >200°. *Anal.* Calcd for $C_4H_{10}SNaAl$: Al, 19.3; Et:Al ratio, 2.00. Found: Al, 18.1; Et:Al ratio, 1.96.

(b) Formation of Complex from XXVI and AlEt$_3$. A mixture of XXVI (1.40 g, 0.01 mol) with AlEt$_3$ (1.37 ml, 0.01 mol) in 5 ml of toluene was refluxed for 8 hr, followed by careful removal of the toluene under moderately reduced pressure to give a concentrated solution from which colorless needle crystals were deposited. These were washed several times with *n*-hexane at −78° and then recrystallized from a concentrated toluene solution. On attempting to determine the melting point, the crystals were found to decompose gradually before melting. *Anal.* Calcd for $C_{10}H_{25}SNaAl_2$: Al, 21.3; Et:Al ratio, 2.5. Found: Al, 20.4; Et:Al ratio, 2.56.

(xxiii) Pentaethyldialuminum Sodiosulfide (XXIVb). One-Step Method. To a suspension of NaSH (4.2 g, 0.075 mol) in 60 ml of toluene was added AlEt$_3$ (21 ml, 0.154 mol), followed by gentle reflux for 12 hr. The reaction mixture was then concentrated by removing toluene under *ca.* 20 mm pressure at room temperature, when the product crystallized out as white needle crystals. These were purified as in part xxiib and were shown to be identical with XXIVa.

(xxiv) Diethyltrimethyldialuminum Sodiosulfide, $[Et_2AlSNa][AlMe_3]$ (XXV). The procedure was as in part xxiib using XXVI (1.40 g, 0.01 mol) with $AlMe_3$ (0.96 ml, 0.01 mol) in 5 ml of toluene. Colorless needle crystals were obtained. *Anal.* Calcd for $C_7H_{19}SNaAl_2$: Al, 25.5; (Et + Me):Al ratio, 2.5; Me:Et ratio, 1.50. Found: Al, 25.0; (Et + Me):Al ratio, 2.4; Me:Et ratio, 1.48.

(xxv) Dissociation of XXIV. (a) The complex XXIV (*ca.* 5 g) was washed five times with 10-ml portions of *n*-hexane at 0°, and 15 ml of toluene was then added. This dissolved nearly all of the solid, and the undissolved residue (*ca.* 0.1 g) was identified as XXVI.

(b) XXIV (*ca.* 2 g) was dissolved in toluene (10 ml), and the solution was allowed to stand for 1 week in a sealed tube at room temperature. During this time a white solid was deposited (*ca.* 0.2 g) which was identified as XXVI.

(c) On heating pure XXIV above 50°, it gradually decomposed.

Infrared spectra were obtained with a Nihon Bunko far-infrared GC-402G instrument, using a compensation technique with a variable-spacing cell. Nmr spectra were measured on a Varian A-60 instrument at room temperature.

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Registry No. $AlMe_3$, 75-24-1; $AlEt_3$, 97-93-8; $Al(i\text{-}Bu)_3$, 100-99-2; LiOH, 1310-65-2; NaOH, 1310-73-2; KOH, 1310-58-3; CsOH, 21351-79-1; PhNHLi, 20732-26-7; $PhCH_2NHLi$, 38225-27-3; *n*-BuNHLi, 41487-32-5; NaSH, 16721-80-5; Me_2AlOLi, 31390-21-3; Et_2AlOLi, 20888-82-8; Et_2AlONa, 31390-22-4; $Et_2AlNPhLi$, 41509-70-0; Et_2AlSNa, 29794-98-7; $[Me_2AlOLi][OC_2H_4]$, 41509-62-0; $[Me_2AlOLi][OEt_2]$, 41509-64-2; $[Me_2AlOLi][O(CH_3)(C_6H_5)]$, 40902-31-6; $[Et_2AlOLi][AlEt_3]$, 15407-37-1; $[Et_2AlONa][AlEt_3]$, 18347-70-1; $[Et_2AlOK][AlEt_3]$, 29467-77-4; $[Et_2AlOCs][AlEt_3]$, 38118-15-9; $[Me_2AlOLi][AlMe_3]$, 18347-68-7; $[(i\text{-}Bu)_2AlOLi][Al(i\text{-}Bu)_3]$, 38194-35-3; $[(i\text{-}Bu)_2AlONa][Al(i\text{-}Bu)_3]$, 38118-18-2; $[Et_2AlOLi][AlMe_3]$, 15492-22-5; $[Et_2AlOLi][Al(i\text{-}Bu)_3]$, 41509-73-3; $[Me_2AlOLi][AlEt_3]$, 41562-78-1; $[Et_2AlONa][AlMe_3]$, 38118-21-7; $[Et_2AlNPhLi][AlEt_3]$, 25136-39-4; $[Me_2AlNPhLi][AlMe_3]$, 15137-70-9; $[(i\text{-}Bu)_2AlNPhLi][Al(i\text{-}Bu)_3]$, 38194-36-4; $[Et_2AlN(CH_2Ph)Li][AlEt_3]$, 15680-63-4; $[Et_2AlN(n\text{-}Bu)Li][AlEt_3]$, 15695-70-2; $[Et_2AlNPhLi][AlMe_3]$, 15694-28-7; $[Et_2AlNPhLi][Al(i\text{-}Bu)_3]$, 41562-79-2; $[Et_2AlSNa][AlEt_3]$, 38118-17-1; $[Et_2AlSNa][AlMe_3]$, 41509-78-8.

Contribution from the Department of Chemistry, The University of British Columbia,
Vancouver 8, British Columbia, Canada

Trifluoromethanesulfonates of Iodine

J. R. DALZIEL and F. AUBKE*

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Iodine tris(trifluoromethanesulfonate), $I(OSO_2CF_3)_3$, is obtained in the oxidation of iodine by stoichiometric amounts of $S_2O_6F_2$ in trifluoromethanesulfonic acid, as a sparingly soluble precipitate. The compound is thermally stable up to +170° and its vibrational spectrum indicates the presence of both monodentate and bidentate bridging SO_3CF_3 groups. Reaction with the stoichiometric amount of iodine at +140° results in the formation of iodine(I) trifluoromethanesulfonate. Several routes to salts of the type $M^I[I(OSO_2CF_3)_4]$, with M^I = K, Rb, or Cs, are also described. Vibrational spectra for these and for $IOSO_2CF_3$ are reported.

(A) Introduction

Reports on the synthesis of trivalent iodine derivatives of strong organic and inorganic protonic acids extend well into the last century.[1] More recent examples of this class of compounds include iodine trisfluorosulfate,[2] $I(OSO_2F)_3$, formed by the interaction of peroxydisulfuryl difluoride,[3] $S_2O_6F_2$, with iodine and iodine trisperchlorate,[4] $I(OClO_3)_3$, synthesized from I_2 and chlorine perchlorate, $ClOClO_3$.[5] Also, iodine tristrifluoroacetate, $I(O_2CCF_3)_3$, has been reported. The compound is obtained *via* a number of synthetic routes.[6-8] This suggests that iodine tris(trifluoromethanesulfonate), $I(OSO_2CF_3)_3$, may also be obtainable.

Structural studies on these compounds are restricted to detailed Raman and some infrared work on $I(OSO_2F)_3$[9] and $I(OClO_3)_3$,[4] suggesting polymeric configurations with both bridging and terminal oxy acid groups, rather than older formulations[1] involving a tripositive iodine cation.

The structural relationship of these compounds to the salts $M^I(IOSO_2F)_4$[10] and $M^I(IOClO_3)_4$[4] was first recognized in the above-mentioned vibrational studies.[4,9] Carter, *et al.*,[9] also report a number of suitable synthetic routes to $[I(OSO_2F)_4]^-$ salts, thus complementing the original method by Lustig and Cady,[10] the interaction of KI with $S_2O_6F_2$. The fairly high thermal stability of these salts again suggests the existence of the $[I(OSO_2CF_3)_4]^-$ analog.

In contrast to the above-described situation for tripositive iodine derivatives, reports on univalent iodine oxy acid compounds are rather limited. The only documented examples are iodine(I) nitrate, $IONO_2$,[11] which is thermally stable only below room temperature, and iodine(I) fluorosulfate,[12,13] $IOSO_2F$. An iodine(I) perchlorate, whose existence as a reaction intermediate has been widely suggested,[14] was found to be rather elusive.[4]

Synthetic efforts to obtain trifluoromethanesulfonic acid derivatives of the three above types are affected by the facts

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