The Amine Complexes of Aluminum Hydride. II

By John K. Ruff and M. Frederick Hawthorne

Indications for formation of *bis*-trialkylamine alanes in solution were obtained, and the stability of the complexes was discussed. Nucleophilic displacement of trimethylamine by the hydride ion from trimethylamine alane has led to a simple preparation of sodium and calcium aluminum hydrides.

In Part I of this series the preparation of several trialkylamine alanes and dialkylamino alanes was reported.[1] The reaction of these materials with some typical Lewis bases was investigated in order to define the conditions for stability of aluminum hydride derivatives in which the aluminum atom exhibits a coördination number of five. A single example is to be found in the literature. The reaction of aluminum hydride with an excess of trimethylamine has been reported by Wiberg[2] to lead to the formation of bis-trimethylamine alane. This material was found to be unassociated in diethyl ether and benzene. However, trimethylamine alane was found to be associated in benzene,[1,2] although it was monomeric in ether. The basicity of the ether is evidently sufficiently strong to form the complex $AlH_3 \cdot N(CH_3)_3 \cdot O(C_2H_5)_2$ at least in solution.

Nucleophilic attack on the amine alanes was generally found to lead to displacement of one Lewis base by another. However, strong indications of complex formation in solution were noted.

Experimental

Aluminum Analysis.[3]—The aluminum sample was weighed into a small flask, and the flask was attached to the vacuum line. Approximately 20 ml. of diethyl ether was condensed into the flask. Then an appropriate amount of methanol was also condensed into the flask. Upon warming the amount of active hydrogen, if any, was determined by a means of a Toepler pump and a calibrated storage bulb system.

The remaining solution was rinsed into a 400 ml. beaker with distilled water and about 10 ml. of 40% sodium hydroxide was added. The mixture was warmed gently to boil off the ether. The aqueous solution was then transferred to a 250 ml. volumetric flask and diluted to the mark with distilled water or dilute sodium hydroxide solution. An aliquot was taken so that it contained approximately 4 mg. of aluminum and placed in a 400 ml. beaker. Two ml. of 10% barium chloride was added to the solution. The *p*H of the solution was adjusted to 11.5 or higher with concentrated sodium hydroxide. It was then brought back to a *p*H of 10.0 by the dropwise addition of 1:1 hydrochloric acid. Then 40 ml. of a 30% anhydrous potassium fluoride solution, whose *p*H had been adjusted to 10.0 with sodium hydroxide, was added. The hydroxide ions released are quantitatively determined by titrating the solution again to a *p*H of 10.0 with standard 0.1 *N* hydrochloric acid solution. The hydrochloric acid solution used in the titration must be specially standardized against pure aluminum since the reaction of the aluminate ion with fluoride ion is not exactly stoichiometric.

Once the requisite solutions were prepared, this method of analysis proved to be extremely rapid without loss of accuracy.

The materials used were sensitive to moisture and oxygen and were handled and stored in a nitrogen filled drybox. All solutions were also prepared in the drybox.

Tensiometric Titrations.—The apparatus consisted of a capillary manometer attached to a tee joint to which a small flask could be fastened. The volume of the apparatus, including the flask, was approximately 70 ml. It was attached to the vacuum line by glass tubing. A solution of 0.2262 g. of trimethylamine alane in 5 ml. of *n*-decane was prepared in the drybox. The flask was attached to the apparatus, cooled to 0° and evacuated thoroughly. Then known amounts of trimethylamine were condensed into the flask with liquid nitrogen. The flask was warmed to room temperature and a water-bath of 25° was placed around it. The pressure was recorded when no further change was noted. A plot of pressure *versus* the molar ratio of amine to amine alane was used to determine the end-point. A sharp break in the curve occurred at a molar ratio of 0.98. The same procedure was used in the titration of triethylamine alane and tri-*n*-propylamine alane with trimethylamine. The end-point in these titrations occurred at ratios of 1.96 and 1.94, respectively.

Molecular Weights.—All the amine alanes used were prepared as described in Part I.[1] The amines were dried over lithium aluminum hydride with the exception of dimethylallylamine. It was dried over barium oxide at reflux overnight.

A different apparatus from that reported previously[1] was used, due to the necessity of having to make successive additions of one component. It consisted of a U tube with connecting cross pieces. One side contained a magnetically driven stirrer, while a Beckmann thermometer, with a ground glass joint, was placed in the other. In order to insulate the apparatus it was placed in a small metal container and packed with glass wool. Reproducibility of the freezing point of benzene was always within ±0.01°.

The general procedure used was to load the apparatus in the drybox with a solution of approximately one gram of the amine alane in 40 ml. of benzene. The apparatus was removed from the drybox and the Beckmann thermometer was put in place under a stream of dry nitrogen. The freezing point was then determined. The thermometer was removed and a known amount of the anhydrous amine was added by means of a weight pipet which was equipped with a ground glass joint. After replacing the thermometer, the freezing point of the mixture was determined. This process was repeated until the mole fraction of the amine alane had been reduced to 0.3 to 0.2. The data below are representative. A solution prepared from 0.828 g. of methyldiethylamine alane and 33.322 g. of benzene showed a freezing point depression of 0.86° which corresponded to a molecular weight of 148. The table below summarizes the data for the addition of methyldiethylamine to the solution described above.

Mole fraction	$CH_3N(C_2H_5)_2$. wt.	ΔT	Mol. wt.
1.00	0.0000	0.86	148
0.85	.1098	0.96	151
.76	.1982	1.04	151
.62	.3719	1.20	153
.52	.5698	1.38	156
.37	1.0623	2.08	139
.28	1.5990	2.95	126
.22	2.2131	4.05	115

Preparation of Lithium Aluminum Hydride.—A 3.0 g. sample of trimethylamine alane was placed in a flask with 1.0 g. of lithium hydride. Approximately 100 ml. of di-

(1) John K. Ruff and M. F. Hawthorne, This Journal, **82**, 2141 (1960). The nomenclature used in this paper is an extension of that proposed in Part I.

(2) E. Wiberg, H. Graf and R. Usón, *Z. anorg. u. allgem. Chem.*, **272**, 221 (1958).

(3) H. L. Watts, *Anal. Chem.*, **30**, 967 (1958).

ethyl ether was condensed into the flask on the vacuum line. After warming to room temperature the mixture was refluxed for 2 hr., during which time considerable amounts of trimethylamine were evolved. The mixture was filtered and the filtrate was evaporated to dryness under vacuum. The residue was extracted with 100 ml. of dry benzene and then the mixture was again filtered. The solid was dried at 60° for several hours under high vacuum. A yield of 0.95 g. was obtained.

Anal. Calcd. for LiAlH$_4$: Al, 71.0; active hydrogen, 10.5. Found: Al, 68.9; active hydrogen, 10.3.

Preparation of Sodium Aluminum Hydride.—A 3.0 g. sample of trimethylamine alane was reacted with 2.0 g. of sodium hydride in 100 ml. of tetrahydrofuran in the manner described above. After refluxing the mixture for 2 hr., it was filtered. The filtrate was evaporated to dryness *in vacuo* and then extracted with 50 ml. of diethyl ether. The solid residue recovered by filtration was dried at 60° for 2 hr. under high vacuum. A yield of 1.4 g. was obtained.

Anal. Calcd. for NaAlH$_4$: Al, 50.00; active hydrogen, 7.4. Found: Al, 50.21; active hydrogen, 7.4.

Preparation of Calcium Aluminum Hydride.—A 2.7 g. sample of trimethylamine alane and with 2.0 g. of calcium hydride were reacted in 150 ml. of tetrahydrofuran. After refluxing for 4 hr. the mixture was filtered. The filtrate was treated as described for the preparation of NaAlH$_4$. The solid obtained was vacuum dried at 60° for 2 hr. A yield of 2.0 g. was obtained.

Anal. Calcd. for Ca(AlH$_4$)$_2$·THF[4]: Al, 30.98; Ca, 23.01; active hydrogen, 4.6. Found: Al, 31.00; Ca, 23.18; active hydrogen, 4.6.

Reaction of NaH with H$_2$Al·N(CH$_3$)$_2$.—A 4.0 g. sample of dimethylamino alane and 3.0 g. of sodium hydride were placed in a flask together with 100 ml. of diethyl ether. The mixture was refluxed for 4 hr. and then filtered. The solvent was removed from the filtrate under reduced pressure and the residue obtained was sublimed at 50°. The sublimate was analyzed.

Anal. Calcd. for HAl[N(CH$_3$)$_2$]$_2$: Al, 23.3; active hydrogen, 0.86. Found: Al, 24.4; active hydrogen, 0.96; H/Al = 1.07.

The ether insoluble residue obtained from the first filtration was extracted with 100 ml. of dry tetrahydrofuran. This mixture was filtered and the solvent was removed from the filtrate *in vacuo*. The residue was dried at 60° for 3 hr. under high vacuum.

Anal. Calcd. for NaAlH$_4$. Al, 50.00; active hydrogen, 7.4. Found: Al, 49.65; active hydrogen, 7.4; H/Al = 3.99.

Results and Discussion

Bis-trialkylamine Alane Formation.—The reactions of amines with trialkylamine alanes or dimethylamino alane fall into two classes. Secondary amines react predominantly as compounds containing acidic hydrogen. Tertiary amines react as Lewis bases, resulting in either displacement or addition.

The formation of bis-trimethylamine alane was demonstrated by a tensiometric titration of trimethylamine alane with gaseous trimethylamine in a constant volume apparatus. No appreciable pressure increase was noted until more than one mole of amine per mole of alane was added. The possible existence of other bis-trialkylamine alanes was investigated briefly by Wiberg.[5] He was unable to prepare bis-triethylamine alane from aluminum hydride and an excess of the anhydrous amine.

In order to determine if any interaction occurred between triethylamine and triethylamine alane,

the mean molecular weight of mixtures of the amine alane and the amine were measured cryoscopically in benzene. Several other amine alanes and the corresponding amines were treated similarly. It was assumed that the presence of the amine did not influence the equilibrium constant for the dimerization reaction of the amine alane The observed

$$2AlH_3 \cdot NR_3 \rightleftharpoons (AlH_3 \cdot NR_3)_2$$
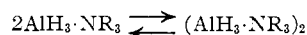
molecular weight of the monomer-dimer mixture of the amine alane was used in the calculations to represent the molecular weight of the mono trialkylamine alane. Figure 1 shows a plot of the difference between the observed molecular weight and the mean molecular weight calculated on the assumption that no interaction occurred between the amine alane and the amine *versus* the mole fraction of aluminum hydride present. Included for comparison are the values calculated for the trimethylamine alane–trimethylamine system assuming complete complex formation. The order of stabilities for the bis-trialkylamine alane complexes found are

$$NR_3 = N(CH_3)_3 > N(CH_3)_2CH_2CH=CH_2 >$$
$$N(CH_3)(C_2H_5)_2 > N(C_2H_5)_3 > N(C_3H_7)_3$$
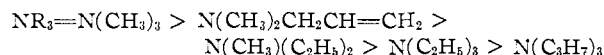
Formation constants of these bis-amine alanes were calculated.[6] They are: AlH$_3$·2N(CH$_3$)$_2$CH$_2$CH=CH$_2$, $K = 2 \times 10^2$, AlH$_3$·2NCH$_3$(C$_2$H$_5$)$_2$, $K = 3$, and AlH$_3$·2N(C$_2$H$_5$)$_3$, $K = 8 \times 10^{-2}$. In the other two cases the interaction was either too strong or too weak to permit calculation.

The observed order of stabilities is just that which would be expected if steric factors were important. The bond hybridization in the bis-amine alanes is most likely sp^{3}d with the nitrogens bonded to the apices of the bipyramid since this configuration is felt to be one of least steric requirements. Measurement of the dipole moment of bis-trimethylamine alane[7] gave a very low value as would be expected for the symmetrical structure. However, if both nitrogens of a difunctional amine were bonded to aluminum in aluminum hydride, two adjacent positions might be occupied.

Even with the nitrogen bonded to the apices, considerable steric interference of the alkyl groups with each other and with the hydrogens is possible, especially for ethyl groups or larger. During the transition from the tetrahedral state of aluminum in the mono amine alane (dimer formation is neg-

(4) A. E. Finholt, *et al.*, *J. Inorg. and Nuclear Chem.*, **1**, 317 (1955), reported that calcium aluminum hydride prepared in THF was obtained as the mono THF etherate.

(5) E. Wiberg and H. Noth, *Z. Naturforschg.*, **106**, 237 (1955).

(6) The expression

$$M = \frac{xM_x + (A - x)M_A + (B - x)M_B}{A + B - x}$$

where x = moles of the complex present
A = stoichiometric concentration of AlH$_3$·NR$_3$ present
B = stoichiometric concentration of NR$_3$ added
M_A = molecular weight of AlH$_3$·NR$_3$ (Note: The value for the monomer dimer mixture was used)
M_B = formula weight of the amine added
M_x = formula weight of the bis-amine complex
M = observed molecular weight
was used to calculate the degree of bis-amine alane formation. The formation constant was then calculated from the expression

$$K = \frac{x}{(A - x)(B - x)}$$

(7) G. Schomburg and E. G. Hoffman, *Z. Elektrochem. Ber., Bunsenges. physik. Chem.*, **61**, 1110 (1957).
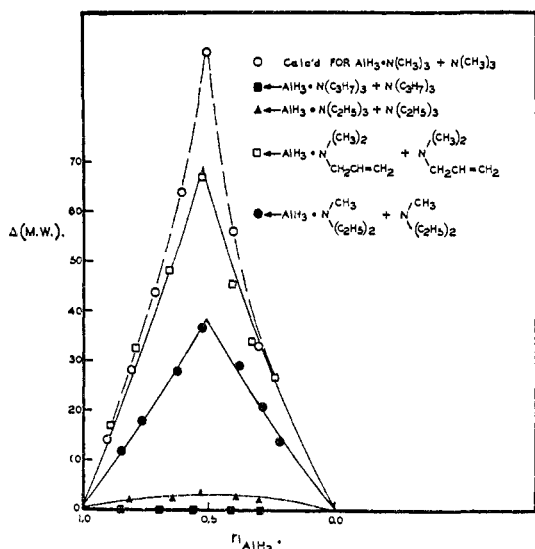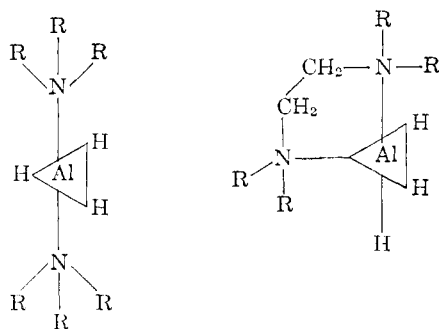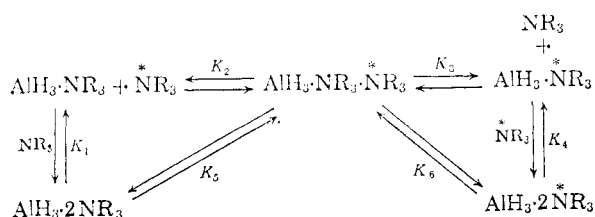
Fig. 1.—The difference between observed molecular weights and that calculated for simple mixtures.

lected) to the penta coördinate state, the hydrogens are forced into a plane bringing them closer to the alkyl groups.

In order to define more closely the steric requirements in the bis-amine alanes, it would be advantageous to compare the equilibrium constants for the reaction of several different amines with a common monoamine alane. However, the introduction of a different amine species considerably complicates the system, if the equilibrium constants for displacement $(K_3/K_2$ in the reaction scheme below) and bis-amine alane formation are similar. The simplified equations below are believed to adequately describe the equilibria involved. Equi-

librium constants K_1, K_2, K_3 and K_4 are written as dissociation constants of a bis-amine alane and K_5 and K_6 are written as formation constants for the mixed bis-amine alane. It is because of this complexity that the determination of relative base strengths of tertiary amines towards the "AlH$_3$"
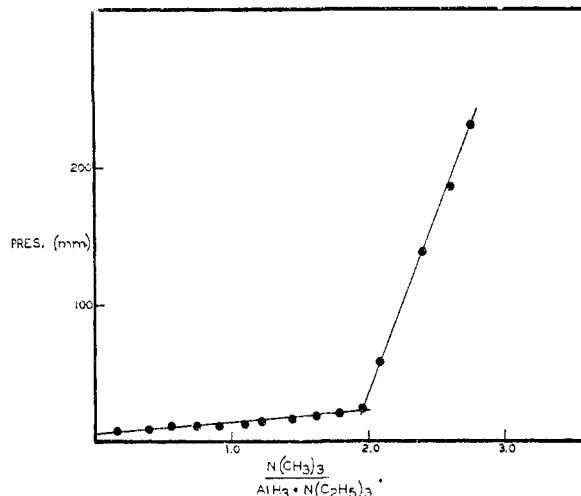

Fig. 2.—Tensiometric titration of triethylamine alane with trimethylamine.

unit by the usual methods is extremely difficult. A true order of basicity can be realized only if the other equilibrium constants are very large when compared to K_2 and K_3. For example, it was found that when triethylamine alane was titrated with gaseous triethylamine, two moles of the latter per mole of alane were immediately consumed (see Fig. 2). Bis-trimethylamine alane was isolated from the reaction mixture. Tri-n-propylamine alane and methyldiethylamine alane exhibited similar behavior when treated with an excess of trimethylamine. The observed displacement of triethylamine, tri-n-propylamine, etc. by trimethylamine does not necessarily mean that the latter is a stronger base toward the "AlH$_3$" unit but could result from the formation of the stable species bis-trimethylamine alane. In other words, due to the very small value for K_1 and a correspondingly large value of K_4, the equilibrium would be continually shifted in the direction of displacement, even if K_2 was larger than K_3. The observed effect would be the liberation of triethylamine.

However, if a system could be found in which K_3 was extremely small compared to K_2, it might be possible to obtain information about K_2. It was felt that the use of trimethylamine alane with other amines would best approximate these conditions. Mean molecular weights for mixtures of trimethylamine alane, with tri-n-propylamine, triethylamine, methyldiethyl amine and dimethylallylamine were determined cryoscopically. A plot of observed molecular weight $versus$ mole fraction of aluminum hydride resulted in curves showing a maximum at a mole fraction of 0.5 for all amines except dimethylallylamine. In this case the maximum appeared at a mole fraction of about 0.7. It is felt that this is due to a value of K_3 which is not small in comparison to K_2 so that some displacement occurs. Using the equations described previously[6] the formation constants of the mixed bis-amine alanes were calculated. They are: AlH$_3$·N(CH$_3$)$_3$N(C$_3$H$_7$)$_3$ K = 7 × 10^{-1}, AlH$_3$·N(CH$_3$)$_3$N(C$_2$H$_5$)$_3$ K = 9 and AlH$_3$·N(CH$_3$)$_3$NCH$_3$(C$_2$H$_5$)$_2$ K = 5 × 10^2. A comparison of these values with the formation

constants of the symmetrical bis-amine alanes shows that the order of stability with the various amines is the same and that the mixed bis-amine alane complexes are more stable. This is to be expected from the steric arguments presented earlier.

Displacement Reactions.—Unlike the analogous boron compound, dimethylamino alane did not react with trimethylamine. Brown has reported a similar example[8] in that no interaction was observed between trimethylamine and dimethylaminodimethylaluminum. Evidently the formation of nitrogen bridges stabilizes the aluminum toward nucleophilic attack. The greatly reduced acidity of the aluminum was again demonstrated in the reaction between dimethylamine and trimethylamine alane.

$$AlH_3 \cdot N(CH_3)_3 + (CH_3)_2NH \longrightarrow$$
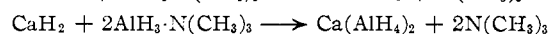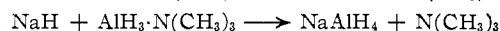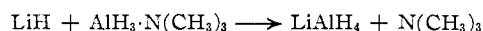$$H_2 + N(CH_3)_3 + H_2AlN(CH_3)_2$$
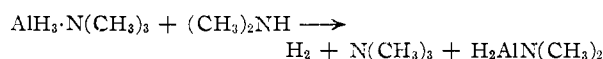
Quantitative yields of hydrogen and trimethylamine were obtained.

The facile displacement of trimethylamine from trimethylamine alane by the dimethylamino group suggested that other strong nucleophiles should behave similarly. Treatment of trimethylamine alane with hydride ion in the form of lithium,

(8) N. Davidson and H. C. Brown, THIS JOURNAL, **64**, 316 (1942).

sodium or calcium hydride resulted in the formation of the metal aluminum hydrides. This method

$$LiH + AlH_3 \cdot N(CH_3)_3 \longrightarrow LiAlH_4 + N(CH_3)_3$$
$$NaH + AlH_3 \cdot N(CH_3)_3 \longrightarrow NaAlH_4 + N(CH_3)_3$$
$$CaH_2 + 2AlH_3 \cdot N(CH_3)_3 \longrightarrow Ca(AlH_4)_2 + 2N(CH_3)_3$$

appears to be a convenient laboratory preparation for sodium or calcium aluminum hydride. The unreacted trimethylamine alane, if any, may be extracted with ether, leaving a product of high purity. Commercial grade magnesium hydride did not react with trimethylamine alane under similar conditions.

Although dimethylamino alane failed to react with trimethylamine, it did react with sodium hydride in a manner analogous to that reported for dimethylamino borane. Disproportionation of the alane occurred with the formation of bis-dimethylamino alane and sodium aluminum hydride
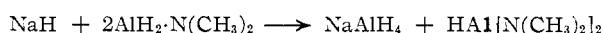
$$NaH + 2AlH_2 \cdot N(CH_3)_2 \longrightarrow NaAlH_4 + HAl[N(CH_3)_2]_2$$

Direct Synthesis of Organotin Compounds. I. Di- and Tribenzyltin Chlorides

BY KEIITI SISIDO, YOSIYUKI TAKEDA AND ZIRÔ KINUGAWA

Benzyl chloride and tin powder suspended in water at 100° gave tribenzyltin chloride, while the same suspension in toluene at 111° afforded dibenzyltin chloride, both in good yields. Over-all equations of the reactions are

$$3C_6H_5CH_2Cl + 2Sn \longrightarrow (C_6H_5CH_2)_3SnCl + SnCl_2 \text{ (in water)}$$
$$2C_6H_5CH_2Cl + Sn \longrightarrow (C_6H_5CH_2)_2SnCl_2 \text{ (in toluene)}$$
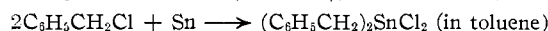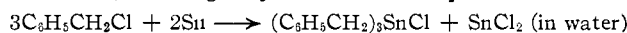
Although the direct syntheses of organotin compounds from the metal and organic halides originated with the second paper of the discovery of this group of substances by E. Frankland[1] and were followed by A. Cahours[2] as well as by T. Karantassis and C. Vassiliadès,[3] the indirect syntheses using a Grignard or other reagent were later found more suitable and were regarded as customary methods.[4] Recent development of the applications of organotin compounds, however, necessitated the revision, and the reactions of halides on

metallic tin are being studied[5] from other point of view.

During the research to extend the Wurtz–Fittig type reaction by iron[6,7] it was found that the action of benzyl chloride on tin powder suspended in water at the boiling point of the medium gave tribenzyltin chloride in a 94% yield calculated on the basis of the halide. The yield of this synthesis far surpassed the known ones.[8-10] Since stannous chloride was obtained from the aqueous layer in a

(1) E. Frankland, *Ann.*, **85**, 329 (1853).

(2) A. Cahours, *ibid.*, **114**, 373 (1860); A. Cahours and E. Demarçay, *Bull. soc. chim. France*, **34**, 475 (1880); *Compt. rend.*, **88**, 1112 (1879).

(3) T. Karantassis and C. Vassiliadès, *ibid.*, **205**, 460 (1937).

(4) For review of literatures not cited here, see E. G. Rochow, D. T. Hurd and R. N. Lewis, "The Chemistry of Organometallic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1957, pp. 182–190, as well as G. E. Coates, "Organometallic Compounds," Methuen & Co., Ltd., London, England, 1956, pp. 118–133. Also an article by R. K. Ingham, S. D. Rosenberg and H. Gilman, *Chem. Revs.*, **60**, 459 (1960).

(5) B. Emmert and W. Eller, *Ber.*, **44**, 2328 (1911); R. W. Leeper, *Iowa State Coll. J. Sci.*, **18**, 57 (1943); H. Gilman and R. W. Leeper, *J. Org. Chem.*, **16**, 466 (1951); A. C. Smith and E. G. Rochow, THIS JOURNAL, **75**, 4103, 4105 (1953); E. G. Rochow, U.S. 2,679,506; *C.A.*, **49**, 4705 (1955); S. Matuda and H. Matuda, *J. Chem. Soc. Japan, Ind. Chem. Section*, **63**, 114 (1960).

(6) K. Sisido, Y. Udô and H. Nozaki, THIS JOURNAL, **82**, 434 (1960).

(7) See also: K. Sisido and H. Nozaki, *ibid.*, **70**, 778 (1948); K. Sisido, H. Nozaki and H. Kuyama, *J. Org. Chem.*, **14**, 1124 (1949).

(8) P. Pfeiffer and K. Schnurmann, *Ber.*, **37**, 319 (1904).

(9) T. A. Smith and F. S. Kipping, *J. Chem. Soc.*, **101**, 2556 (1912).

(10) M. M. Nad and K. A. Kocheshkov, *J. Gen. Chem. U.S.S.R.*, **8**, 42 (1938); *Chem. Zentr.*, **100**, I, 2175 (1939).