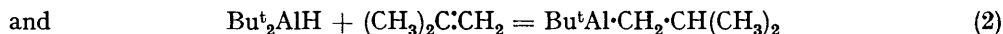


### 531. The Synthesis of Tri-*t*-Butylaluminium–Diethyl Ether Complex.

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The conditions for the synthesis of tri-*t*-butylaluminium–diethyl ether complex by reaction of *t*-butyl–lithium with aluminium trichloride in ether solution have been studied. Particular attention has been paid to the absence of products formed as a result of rearrangement of the *t*-butyl groups.

CONSIDERABLE interest has been shown recently in the preparation and properties of organoaluminium compounds,<sup>1</sup> though preparation of *t*-butylaluminium compounds does not appear to have been reported. The present investigation is concerned with preparation of tri-*t*-butylaluminium–ether complex and a study of some of its outstanding properties. Particular attention has been paid to the possibility of rearrangement of the *t*-butyl groups during some process involved in the synthesis.<sup>1</sup> Such a rearrangement can be represented as follows:



These reactions may then proceed until all the *t*-butyl groups have rearranged to isobutyl groups.

In this connexion it has been pointed out<sup>1</sup> that synthesis of tri-*t*-butylaluminium by reaction of a compound containing the AlH group with olefins is not possible. Furthermore, tri-isopropylaluminium rearranges to tri-*n*-propylaluminium on being heated to 110–130°.

As a result of extensive studies on the decomposition and exchange reaction of trialkylaluminium compounds Ziegler *et al.*<sup>2</sup> have suggested that with long-chain alkyl groups some dialkylaluminium hydride is always present. Molecular-weight measurements show that complexes of the type  $\text{R}_3\text{Al}\cdot\text{R}_2\text{AlH}$  are formed. Because of the equilibria of the type shown by equations (1) and (2) it is impossible to prepare pure  $\text{R}_3\text{Al}$  and an increase of temperature increases the degree of dissociation. Thus, for tri-isobutylaluminium the degree of dissociation is 8.4, 9.0, and 11.6% at 80, 100, and 120°, respectively, and at 150° the removal of 1 mole of isobutene is complete, the remaining di-isobutylaluminium hydride decomposing to aluminium, isobutene, and hydrogen at 250°.<sup>3</sup>

Various methods have been described for detection and determination of dialkylaluminium hydrides.<sup>4,5</sup> In particular the infrared absorption and degree of association of dialkylaluminium hydrides have been studied by Hoffmann and Schomburg,<sup>6</sup> who found that the AlH group gives an intense and broad absorption in the 1800  $\text{cm}^{-1}$  region and a sharp, less intense band at 750  $\text{cm}^{-1}$ . It was established that samples of tri-*t*-butylaluminium–ether complex gave no absorption at 1800  $\text{cm}^{-1}$ . Treatment, however, of the sample in benzene with benzylideneaniline<sup>5</sup> gave a transient red colour indicating the presence of small amounts of hydride, in keeping with Ziegler's comments.

Absence of products formed as a result of rearrangement of *t*-butyl groups was shown by two methods. First, a sample of *t*-butylaluminium–ether complex was subjected to autoxidation.<sup>7</sup> This was followed by hydrolysis of the alkoxide and extraction of the

<sup>1</sup> Ziegler, "Organometallic Chemistry," edited by H. Zeiss, A.C.S. Monograph Series No. 147, 1960.

<sup>2</sup> Ziegler, Kroll, Larbig and Steudel, *Annalen*, 1960, **629**, 53.

<sup>3</sup> Ziegler and Gellert, *Angew. Chem.*, 1955, **67**, 424.

<sup>4</sup> Ziegler and Gellert, *Annalen*, 1960, **629**, 20.

<sup>5</sup> Neumann, *Annalen*, 1960, **629**, 23.

<sup>6</sup> Hoffmann and Schomburg, *Z. Elektrochem.*, 1957, **61**, 1101.

<sup>7</sup> Davies and Hall, *J.*, 1963, 1192.

alcohols by benzene. By gas chromatographic methods t-butyl alcohol and diethyl ether were found, but no other alcohol. Secondly, the total reaction mixture was treated with stannic chloride to convert the alkyl group into a stable alkyltin(IV) compound which could be conveniently handled. It was assumed that no alkyl group isomerisation had taken place during the preparation of the alkyltin(IV) compound, the n.m.r. spectrum of which was observed. A single-line signal was obtained the position of which was determined by comparison with tetramethylsilane. If isobutyl groups were present a more complex spectrum would be obtained capable of detecting 5% isobutyltin(IV) product. Therefore to within this limit t-butyl accounted for all the alkyl groups present in the mixture. An unusual feature of the interaction of the product mixture with stannic chloride was the appearance of stannous chloride. This originally was thought to be due to the presence of substantial amounts of dialkylaluminium hydride in the mixture. A recent investigation<sup>8</sup> has shown that reaction of stannic chloride with di-isobutylaluminium hydride gives rise to stannous chloride as one of the major products. Reaction, however, of the tri-t-butylaluminium-ether complex with stannic chloride gave the same quantity of stannous chloride. It may be argued that this could be due to pre-equilibrium formation of hydride, as shown by equation (1) followed by reaction of the hydride to form stannous chloride. If the reaction was carried out at  $-10^{\circ}$  a brown solid separated which subsequently decomposed at room temperature. This could possibly be due to an unstable t-butyl alkylation product of stannous chloride. In this connexion it may be noted that reaction of trialkylaluminium compounds with stannous chloride has become an established synthetical route to organotin(IV) derivatives though in no case has the formation of stannous chloride been reported.

The absence of rearrangement of the t-butyl groups in tri-t-butylaluminium-ether complex is in marked contrast to similar compounds of boron. The studies of McCusker *et al.*<sup>9</sup> reveal that formation of di-isobutyl-t-butylborane from reaction of boron fluoride with t-butylmagnesium chloride requires isomerisation of two of the three t-butyl groups during synthesis. The mechanism suggested involves the reducing reaction of sterically hindered Grignard reagent on the alkylfluoroborane resulting in the formation of alkylboron hydride and olefin. The olefin then adds to the B-H bond to form the isobutyl group. A comparable case is the reaction of t-butylmagnesium chloride with triphenylsilyl chloride, to form triphenylsilane and the corresponding olefin.<sup>10</sup> Further, it was observed that di-t-butylboron hydride adds rapidly to a normal terminal olefin but can add slowly or not at all to a branched chain olefin.

The t-butyl group of tri-t-butylaluminium-ether complex undergoes thermal decomposition to form the AlH group. It has been noted by Zeigler<sup>1</sup> that the ease of reaction of the AlH group with olefins decreases in the order  $\text{CH}_2=\text{CH}_2 > \text{R}\cdot\text{CH}=\text{CH}_2 > \text{R}_2\text{C}=\text{CH}_2$ . Evidently the rate of reaction of isobutene with di-t-butylaluminium hydride-ether complex is too slow for any appreciable amount of isobutyl di-t-butylaluminium-ether complex to form. Coates and Glockling<sup>11</sup> were able to prepare beryllium hydride by thermal decomposition of di-t-butylberyllium and elimination of isobutene.

#### EXPERIMENTAL

All transfer operations were carried out under nitrogen and manipulations of samples done in a dry box under nitrogen.

*The Addition of Aluminium Trichloride to t-Butyl-lithium.*—Pure aluminium trichloride was prepared by passing hydrogen chloride over AnalaR aluminium wire at about  $500^{\circ}$ , and separated by sublimation. t-Butyl-lithium was prepared by the method of Bartlett and Lefferts<sup>12</sup> from finely divided lithium (5.6 g.) and t-butyl chloride (46 ml.), the total volume of

<sup>8</sup> Smith, *Nature*, 1963, **199**, 374.

<sup>9</sup> McCusker, Marra, and Hennion, *J. Amer. Chem. Soc.*, 1961, **83**, 1924.

<sup>10</sup> Harvey, Nebergall, and Peake, *J. Amer. Chem. Soc.*, 1957, **79**, 2762.

<sup>11</sup> Coates and Glockling, *J.*, 1954, 2526.

<sup>12</sup> Bartlett and Lefferts, *J. Amer. Chem. Soc.*, 1955, **77**, 2804.

2772 *The Synthesis of Tri-*t*-butylaluminium–Diethyl Ether Complex.*

ether being 300 ml., and the reaction mixture cooled to  $-40^{\circ}$ . An ether solution of aluminium trichloride (11.0 g. in 100 ml.) was added slowly so that the temperature did not rise above  $-35^{\circ}$  (sudden addition of the aluminium trichloride caused a temperature rise of about  $25^{\circ}$  in the mixture). Thereafter the mixture was kept at this temperature for 8 hr., brought to room temperature, filtered under nitrogen through a No. 3 glass sinter and most of the ether removed by distillation at diminished pressure. The temperature was raised to  $50^{\circ}$  and pumping continued for about 2 hr. Cold water was circulated through a cold finger fitted to the vessel and pumping at  $1.0 \times 10^{-2}$  mm. continued for 2 days, when tri-*t*-butylaluminium–ether complex (4 g.) collected on the cold finger. Finally the cold finger was isolated from the filtration vessel and further pumped for 2 days. Samples for investigation were then removed from the cold finger in a dry box.

*Gas Chromatographic Determination of the Ether and *t*-Butyl Content of the Tri-*t*-butylaluminium–Ether Complex.*—The gas chromatographic equipment employed an argon ionisation detector and was assembled from commercially available components. The liquid phase used was dinonyl phthalate 14 on a G-cel solid support (60–80 mesh), the flow rate being 10.0 ml./min., on a 2-ft. column.

Samples of the trialkylaluminium–ether complex were taken up in benzene and treated with dry oxygen until no further uptake occurred. The benzene solution of the resulting alkoxide was equilibrated with dilute sulphuric acid saturated with AnalaR aluminium sulphate. The alcohol and ether present were identified by comparison of retention times with known samples of alcohols and diethyl ether. Only three peaks were obtained, due to benzene, *t*-butyl alcohol and diethyl ether. Quantitative determinations of ether present were carried out by comparison with standard amounts equilibrated with sulphuric acid saturated with aluminium sulphate. It was found that the method gave reproducible results for the estimation of ether present, corresponding to  $0.83 \pm 0.05$  mole of ether present for each mole of trialkylaluminium.

*Hydrolysis of Tri-*t*-butylaluminium–Ether Complex.*—Samples of the trialkylaluminium were weighed out, treated with a little methanol, and finally dissolved in acetic acid. The lithium content of the resultant solution was examined by an EEL flame photometer using a lithium filter. The solution obtained from the hydrolysis of the alkylaluminium was thus shown to be substantially free from lithium. Similarly, treatment of the solution with silver nitrate indicated the absence of chloride. The aluminium content of the product was determined by gravimetric estimation of the aluminium as the 8-hydroxyquinolate [Found: Al, 10.5, 10.4.  $(C_4H_9)_3Al, 0.83O(C_2H_5)_2$  requires Al, 10.4%].

*Reaction of the Alkylaluminium Mixture with Stannic Chloride.*—An ethereal solution of the *t*-butylaluminium mixture was prepared as previously described. Most of the ether was removed and sodium-dried cyclohexane (100 ml.) was added to the residue, and the solution filtered under nitrogen. The cyclohexane was removed at diminished pressure at  $50^{\circ}$ , the distillation vessel was filled with nitrogen, and the residue was treated with cyclohexane (100 ml.) and again filtered. A small amount of white solid remained which dissolved readily in methanol. It gave positive reactions for chloride and lithium though a quantitative determination indicated more lithium than could be accounted for by lithium chloride. It is tentatively suggested that it could be an alkyl lithiumaluminium though further characterisation was not carried out. To the cyclohexane filtrate a solution of stannic chloride (10 g.) in cyclohexane was slowly added with rapid stirring. The mixture was heated under reflux for 4 hr. cooled to room temperature, and filtered through a No. 3 glass sinter. The white precipitate which remained on the sinter was washed with cyclohexane ( $2 \times 100$  ml.) and transferred into ether (100 ml.), and the solution filtered. The residue (2 g.) was then heated to  $160^{\circ}$  at reduced pressure for 2 hr. A solution of this residue in hydrochloric acid gave an immediate violet coloration with cacotheline and the stannous content determined by titration with standard iodine solution [Found: Sn, 62.1; Cl, 37.0.  $SnCl_2$  requires Sn, 62.6; Cl, 37.4%]. A similar amount of stannous chloride was obtained from reaction at room temperature.

The n.m.r. spectrum of the cyclohexane solution of organotin compounds was recorded, tetramethylsilane being used as standard.<sup>13</sup> The spectrum observed consisted of a single line with  $\tau$  9.06. It follows that the alkyl groups in the organotin chloride were *t*-butyl groups.

The cyclohexane solution was washed with 4*N*-hydrochloric acid (100 ml.), separated, and

<sup>13</sup> Tiers, *J. Phys. Chem.*, 1958, **62**, 1151.

[1964]

Boller and Whitfield.

2773

dried ( $\text{CaCl}_2$ ). Ether (100 ml.) was added and the solution treated with hydrogen chloride. The solvents were removed by distillation, leaving a residue (3.5 g.) which consisted mainly of tri-*t*-butyltin(IV) chloride<sup>14</sup> [Found: C, 44.6; H, 8.3, Cl, 10.9.  $(\text{C}_4\text{H}_9)_3\text{SnCl}$  requires C, 44.9; H, 8.4; Cl, 11.1%].

*Infrared Spectrum of the Trialkylaluminium.*—The infrared spectra were recorded by using sodium chloride optics and variable-path liquid cell. The infrared spectrum of the tri-*t*-butylaluminium-ether complex was recorded in cyclohexane solution and there was no evidence of hydride present. For comparison, and in order to confirm the measurements made on the cyclohexane solution of tri-*t*-butylaluminium-ether complex, the spectrum of di-*isobutyl*-aluminium hydride was recorded.

*Colorimetric Detection of Di-*t*-butylaluminium Hydride.*—This was carried out by use of benzilideneaniline as described.<sup>5</sup> Calibration curves were constructed from benzene solutions of di-*isobutyl*aluminium hydride by using a Unicam S.P. 500 spectrophotometer at 500 m $\mu$ . It has previously been noted<sup>15</sup> that the extension coefficient of the coloured complex formed is independent of the alkyl group present so that the calibration curves could be used for the estimation of di-*t*-butylaluminium hydride present in various mixtures.

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<sup>14</sup> Krause and Weinberg, *Ber.*, 1930, **63B**, 381.

<sup>15</sup> Ray, *J. Appl. Chem.*, 1954, **4**, 21.

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