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THE QUESTION OF ALLYLIC REARRANGEMENT IN THE REACTIONS OF TRIBENZYLALUMINUM*

JOHN J. EISCH AND JEAN-MICHEL BIEDERMANN
Maloney Chemical Laboratory, The Catholic University of America, Washington, D.C. 20017 (U.S.A.)
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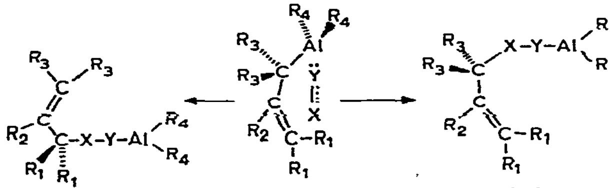
SUMMARY

In order to evaluate the structural factors leading either to normal or to allylic reactions with allylic carbon–aluminum bonds, the behavior of pure samples of tribenzylaluminum and of tribenzylaluminum diethyl etherate has been examined. Analysis of their NMR spectra as a function of temperature between +25° and −90° was consistent with the presence of monomeric, non-fluxional species. Their cleavage reactions under agency of deuterium oxide, diphenylacetylene, or ultraviolet radiation proceeded normally, while that with carbon dioxide occurred only with allylic rearrangement. The case of benzophenone anil was one where principally normal cleavage, succeeded by an elimination reaction, was observed.

INTRODUCTION

The highly covalent character of the carbon–metal bond in Group IIIB organometallic compounds, coupled with their Lewis acidity, often determines that an intermediate complex (I) with a reactant (X=Y:) will be formed before final reaction [eqn. (1)][2]. Observable complexes between organoaluminum compounds and amines (R_nNH_{3-n}, where $n=0$–2)[3], nitriles[4] or carbonyl derivatives[5,6] are cases in point, although no such complexes have as yet been observed with olefinic or acetylenic substrates[7]. In organoaluminum reagents of the allylic or benzylic type such an intermediate complex could decompose, either with normal reaction (II) or with allylic rearrangement (III).



(III) (I) (II)

(1)

The chemical behavior of allylic and benzylic aluminum compounds has been

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* Part XVIII of the series "Organometallic Compounds of Group III"; previous related parts, see ref. 1.

little explored; only in recent years have such compounds been prepared in the pure state. Benzylaluminum reagents have been prepared in solution by the interaction of aluminum chloride with benzyl Grignard reagent, but the mixture was used without separation or purification[8]. Benzylic compounds, previously thought to be of the 7-aluminabicyclo[2.2.1]heptadiene type[9], have been prepared but crystallographic structure determination now shows them to be dimeric and to contain 10-membered aluminum heterocyclic rings[10]. Recently also, a benzylic aluminum adduct was obtained from the addition of diisobutylaluminum hydride to the 1,2-bond of acenaphthylene[11], and tribenzylaluminum itself was prepared from the exchange between tribenzylborane and triethylaluminum[12]. Finally, the synthesis of allylaluminum etherates has now been achieved[13]. Since our earlier work on the behavior of allylic aluminum compounds showed that both normal carbon–aluminum bond cleavage and cleavage with allylic rearrangement could occur[11], we judged that an examination of the chemistry of tribenzylaluminum, as well as its etherate, would be useful in defining the structural factors leading to normal or allylic cleavage reactions. A further advantage in such a study is that the molecular structure of tribenzylaluminum itself and that of its etherate could be examined by NMR spectroscopy. In this way any fluxional character[14] leading to a benzylaluminum/*o*- (or *p*-)tolylaluminum group interconversion could be ruled out as the cause of any observed allylic rearrangement.

RESULTS AND DISCUSSION

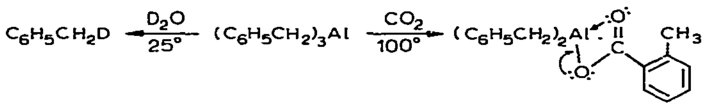
The preparation of unsolvated tribenzylaluminum from aluminum metal and the readily preparable[15] and commercially available dibenzylmercury proved more convenient than the known exchange between tribenzylborane and triethylaluminum[12]. The temperature of the aluminum–mercury exchange reaction had to be maintained at < 120° [80% yield in refluxing toluene, eqn. (2)], in order to avoid the predominant thermolysis of dibenzylmercury which ensued in refluxing xylene. Although the diethyl etherate could be obtained from the tribenzylaluminum so prepared, this complex could also be satisfactorily prepared from the interaction of aluminum chloride and three equivalents of benzylmagnesium chloride in ethyl ether solution [eqn. (3)]. In fact, the pure tribenzylaluminum diethyl etherate obtained in this manner could not easily be freed of its complexed ether without concomitant destruction of carbon–aluminum bonds.

$$3(C_6H_5CH_2)_2Hg + 2Al \xrightarrow{<120°} \underset{(IV)}{2(C_6H_5CH_2)_3Al} + 3Hg \qquad (2)$$

$$3C_6H_5CH_2MgCl + AlCl_3\cdot(C_2H_5)_2O \rightarrow \underset{(V)}{(C_6H_5CH_2)_3Al\cdot O(C_2H_5)_2} + 3MgCl_2 \qquad (3)$$

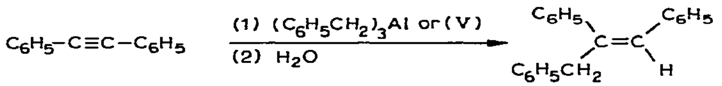
The NMR spectra of tribenzylaluminum(IV) and its etherate(V) in toluene-d_8 showed proton resonance patterns expected for σ-bonded, non-fluxional benzylaluminum groups. In addition, the maintenance of a single, unshifted benzyl peak in (IV) while the temperature was varied between +25° and −90° is consistent with the existence of tribenzylaluminum as a monomeric, σ-benzyl system under these conditions. If rapid exchange of bridging and non-bridging benzyl groups in dimeric tribenzylaluminum were responsible for the averaged benzyl singlet at $+25^\circ$, lowering the temperature should have revealed two benzyl resonances. Even dimeric trimethylaluminum reveals its two expected methyl signals at -75°[16].

The chemical behavior of both tribenzylaluminum and its etherate was investigated individually toward deuterium oxide, toward carbon dioxide and toward diphenylacetylene. No difference in chemical response was noted between the unsolvated organoaluminum reagent(IV) and the etherate(V), which is stable to thermal dissociation into (IV) under the reaction conditions. Action of an excess of deuterium oxide on (IV) or (V) at room temperature gave only α-deuteriotoluene (VI) and, therefore, only the normal cleavage [eqn. (4)]. Gaseous carbon dioxide at 100° under normal pressure, however, yielded only the allylic rearrangement product, *o*-toluic acid; furthermore, the crude yield of 31–33 % showed that only one benzyl–aluminum bond responded under these conditions. The stabilizing influence of oxygen coordination [(VII), intramolecularily or through its dimer] may sharply diminish the Lewis acidity of the aluminum center toward further CO_2 insertion [eqn. (4)].

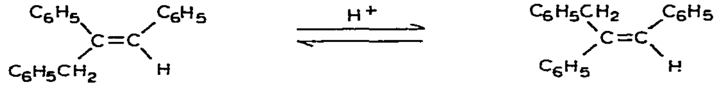

(4)

(VI) (IV) or (V) (VII)

Extensive studies in this laboratory of the addition of carbon–aluminum bond to olefins and acetylenes[1] made the behavior of diphenylacetylene toward (IV) and (V) of keen interest. Only one mode of addition was observed, namely the normal addition of the benzyl–aluminum bond in a *cis*-fashion [eqn. (5)]. Although two isomers of the resulting 1,2,3-triphenylpropene have been described[17,18], identification of the stereochemical character of the reaction product as isomer(VIII) had to be made by isomerizing it with acid to a mixture of two isomers (VIII) and (IX) [eqn. (6)], separating isomer (IX) and measuring its NMR spectrum. By means of recent empirical chemical shift relations[19], isomer (VIII) was confirmed to be the *cis*-1,2-diphenyl, isomer (IX) the *trans*-1,2-diphenyl, derivative.


(VIII)

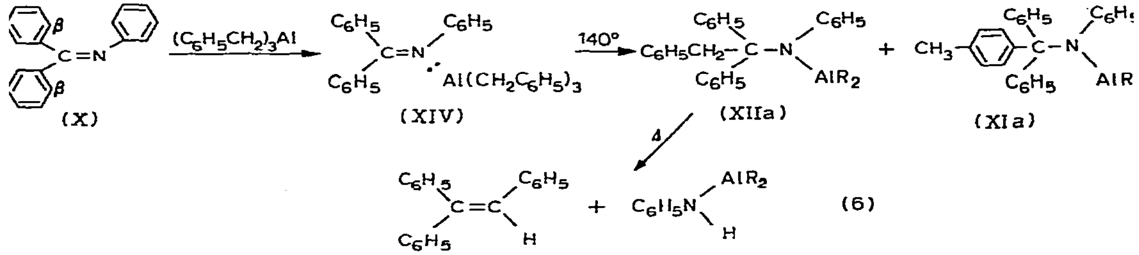
(5)


(6)

(VIII) (isomer A) (IX) (isomer B)

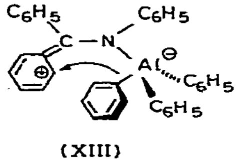
The response of unsolvated tribenzylaluminum(IV) to benzophenone anil(X) was of two-fold interest, namely to learn whether(IV) would form an adduct of the benzyl or of the tolyl type and also to see whether the anil(X) itself would undergo 1,2- or 1,4-addition. Although the color change accompanying the admixture of (IV) and (X) showed that at least a complex was formed, a 72 h-reflux period in benzene followed by hydrolysis led to a complete recovery of the unchanged anil. Only upon heating a xylene solution of (IV) and the anil at reflux for 5 days was addition achieved and even then 65% of the anil was recovered upon hydrolysis. The balance of the reaction product consisted of ca 20% of triphenylethylene, 5% of *N*-(diphenyl-*p*-tolylmethyl)aniline (XI), 2% of *N*-(benzyldiphenylmethyl)aniline (XII) and aniline. No benzhydrylaniline or *N*-(diphenyl-*o*-tolylmethyl)aniline was detected by NMR analysis, although small amounts of unidentified products (< 1%) were present. Based upon the behavior of triphenylaluminum, the absence of benzhydrylaniline tends to rule out any attack of IV at the β-position of (X). Like (IV), triphenylaluminum does attack (X) in refluxing xylene, but only at the β-position; the adduct readily loses $(C_6H_5)_2AlH$ and this hydride attacks the unreacted anil (X), leading to benzhydrylaniline and an *ortho*-phenylated benzophenone anil upon hydrolysis[20].

All the products from the anil and tribenzylaluminum point to an exclusive 1,2-addition to the azomethine linkage. The *p*-tolyl adduct (XIa) shows that a small amount of addition did occur with benzylic rearrangement, but the triphenylethylene undoubtedly is a thermal transformation product of the *N*-(benzyldiphenylmethyl)-aniline adduct (XIIa):

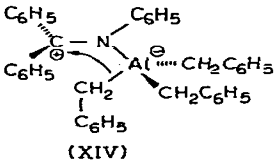


(6)

As with the corresponding magnesium compounds[21,22], phenyl–aluminum bonds add only in 1,4-fashion to benzophenone anil, while benzyl–aluminum bonds add only in a 1,2 manner. One could well advance a steric argument as to why tribenzylaluminum could more ready add 1,2 than its phenyl counterpart. In refluxing xylene, however, where both aluminum compounds attack the anil slowly, it is hard to accept a steric reason for the failure of any of the benzyl to add 1,4. An electronic mechanistic difference seems more reasonable. The initial complex of (X) with triphenylaluminum would polarize the β-position which then could behave as an electrophile toward the aromatic–aluminum bond (XIII); the initial complex of (X) with tribenzylaluminum cannot form a similar six-membered transition state with the β-position and a bond highly prone to electrophilic attack, namely a vinylic–aluminum bond. The superior anionic stability of the benzyl group, compared with that of the phenyl group, seems rather to promote the anionic migration to C_2 and, hence, 1,2-addition (XIV) of either a benzyl or a *p*-tolyl group:



(XIII)



(XIV)

The photo-lability of tribenzylaluminum in benzene solution was examined in an exploratory manner. In a very slow photolysis aluminum metal and bibenzyl were formed as the principal products. Treatment of the reaction solution with deuterium oxide led to the isolation of toluene monodeuterated only at the α-position (VI). From this it is concluded that no detectable allylic isomerization of benzyl–aluminum bonds to tolyl–aluminum bonds occurred upon irradiation.

EXPERIMENTAL

The usual techniques for exclusion of oxygen and moisture were involved in the preparation and manipulation of organometallic reagents. All organometallic reactions were maintained under an atmosphere of dry, oxygen-free nitrogen until they were worked up by treatment with water and/or gaseous carbon dioxide. Hydrocarbon solvents were dried by refluxing over and distilling from calcium hydride; commercially available anhydrous ether was used directly.

Infrared spectra were recorded on a Perkin–Elmer spectrophotometer, model 337; mass spectra with a Varian–Atlas instrument, model CH-5; and NMR spectra with a Varian spectrometer, model A-60. The NMR spectral data are reported in the δ-scale (ppm downfield from internal tetramethylsilane). The melting points were taken in capillaries, sealed under nitrogen where necessary, and are uncorrected.

Preparation of tribenzylaluminum diethyl etherate (V)

A solution of 63.0 g (0.498 mole) of reagent-grade benzyl chloride dissolved in 90 ml of diethyl ether was added with vigorous stirring over a period of two h to a suspension of 14.0 g (0.577 g-atom) of magnesium turnings in 150 ml of ether. (The magnesium turnings had been previously ground with small crystals of iodine). By titration of a hydrolyzed aliquot with standard acid, the yield of Grignard reagent was 85%.

Pure, freshly sublimed aluminum chloride (18.9 g, 0.142 mole) was dissolved with cooling in 200 ml of ether and the resulting solution treated with the foregoing Grignard reagent over a 30 min period. The suspension was stirred overnight at 25° and then heated at reflux for three h. Dry benzene (200 ml) was added and the reaction suspension heated to distill off the majority of the ether. The benzene suspension was filtered through a glass frit of medium porosity and the filtrate was freed of benzene and ether under reduced pressure (final heating at 160°). The residue was extracted with 200 ml of xylene to leave behind any remaining aluminum salts. The xylene extracts were again filtered and freed of solvent *in vacuo*. The residue was then extracted several times with hot heptane. By cooling the extracts in a solid CO_2-acetone bath colorless crystals of tribenzylaluminum diethyl etherate were formed. Three recrystallizations from heptane and drying under vacuum gave 18.1 g (34% yield) of pure product, m.p. 48–50°. The yield of product of practical purity was considerably higher. (Found: Al, 7.27. $C_{25}H_{31}AlO$ calcd.: Al, 7.21%.) NMR (C_6D_6; δ(ppm), no. H, multiplicity and J(Hz): 0.42, 6H, triplet, 7; 1.74, 6H singlet; 3.1, 4H, quartet, 7; 6.83–7.36, 15H, multiplet.

Treatment with deuterium oxide. A solution of 1.5 g (4.0 mmole) tribenzylaluminum diethyl etherate in 15 ml of dry hexane was treated by means of a hypodermic syringe through a septum in the reaction vessel, with 1.0 ml of deuterium oxide (99.8%

pure). After a 30 min stirring period, the resulting suspension was filtered and the filtrate dried over anhydrous calcium sulfate. The toluene was isolated by distillation of the hexane solution through a 40 x 2 cm spinning band column. The NMR spectrum in CCl_4 of the isolated toluene had a triplet whose components had equal intensity at 2.28 (2H) and essentially a singlet at 7.09 (5 H). Thus, only α-deuteriotoluene (VI) was formed upon hydrolysis.

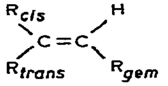
Treatment with carbon dioxide. A solution of 1.48 g (4.0 mmole) of the aluminum compound in 20 ml of heptane was treated at the reflux temperature and over a 5 h period with a slow stream of dry carbon dioxide gas. The cooled mixture was hydrolyzed with dilute sulfuric acid and the organic fraction extracted into 100 ml of ether. After drying over anhydrous calcium sulfate the ether extracts were freed of volatile solvent at the rotary film evaporator. An NMR ($CDCl_3$) examination of the resulting crude solid acid (0.50 g) showed only the methyl singlet at 2.68 ppm, characteristic of *o*-toluic acid, and no signal at 3.11 ppm, which would be expected for phenylacetic acid. Other signals for *o*-toluic acid at 7.1–7.5 (m), 7.95–8.18 (m, C–H *ortho* to COOH) and at 11.7 ppm (COOH) were observed in their expected intensities. Recrystallization from water gave colorless crystals, m.p. 99–102° (lit. 103.7°). The yield of crude, essentially pure acid was 31 %.

Treatment with diphenylacetylene. When a solution of 1.9 g (5.1 mmole) of the aluminum compound and 0.90 g (5.1 mmole) of diphenylacetylene in 20 ml of heptane was refluxed for 3 days, no reaction occurred, as shown by VPC examination of a hydrolyzed aliquot. By distillation the heptane was replaced by xylene and the xylene solution then heated under reflux for 2 days. A hydrolyzed aliquot now showed that the diphenylacetylene had been consumed. Hydrolytic work-up, extraction of the organic product into ether, drying over anhydrous calcium sulfate and solvent removal yielded 1.1 g (80 %) of a pale yellow solid, whose NMR (CCl_4) spectrum showed to be essentially 1,2,3-triphenylpropene (3.7, doublet, 2 H, 1 Hz; 6.38, triplet, 1 H, 1 Hz; 6.85–7.55, multiplet), but that a small amount of bibenzyl (2.83 ppm) was present. No significant signal attributable to a methyl group of a 1,2-diphenyl-1-*o*-tolylethylene could be observed. Recrystallization of this product from n-butyl alcohol gave colorless needles[17], m.p. 60–61°. NMR (CCl_4) data: 3.74, d, 2 H, 1 Hz; 6.41, (br)trip., 1 H; 6.9–7.2, m, 15 H.

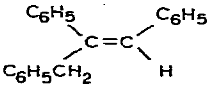
Whether this 1,2,3-triphenylpropene was *cis*-1,2-diphenyl (VIII) or *trans*-1,2-diphenyl (IX) was decided by an acid-catalyzed isomerization and an NMR study. This homogeneous compound was dissolved in warm glacial acetic acid containing several drops of concentrated sulfuric acid and the solution warmed for four h on the steam bath. The cooled solution was made basic with aqueous sodium hydroxide solution and the organic phase extracted into ether. After separation the ether extract was washed with water, dried over anhydrous calcium sulfate and then freed of solvent. The recovered triphenylpropene was shown by vapor phase chromatography to consist of two peaks in a ratio of 1/1. One of the peaks was the original 1,2,3-triphenylpropene isomer (A), as shown by its VPC isolation and NMR identification. The other isomer (B)[18] showed, upon VPC separation, the following NMR spectrum (CCl_4): 4.08, singlet, with sl. sh, 2 H; 7.07, (br) singlet, 1 H; 7.15–7.5, multiplet 15 H. The following expression was used to calculate the expected chemical shift of the vinyl C–H:

$\delta(C{=}C{-}H) = 5.25 + Z_{gem} + Z_{cis} + Z_{trans}$

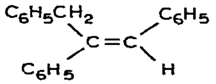
where $Z =$



For the *cis*-1,2-diphenyl isomer, $\delta(C{=}C{-}H) = 5.25 + 1.38 - 0.29 - 0.07 = 6.27$



(A) *cis* -1,2-diphenyl isomer (VIII)



(B) *trans* – 1,2 – diphenyl isomer (IX)

For the *trans*-1,2-diphenyl isomer, $\delta(C{=}C{-}H) = 5.25 + 1.38 + 0.36 - 0.32 = 6.67$. The actual values of 6.41 for isomer (A) and 7.07 for isomer (B) lead us to assign the *cis*-1,2-diphenyl configuration to isomer (A), and the *trans*-1,2-diphenyl configuration to isomer (B). Moreover, the observed, larger splitting of the vinylic and benzylic hydrogens by each other ($\sim$1 Hz) in isomer (A) is also consistent with this assignment. Thus, it is concluded that carbalumination of diphenylacetylene by tribenzylaluminum etherate occurs exclusively in a *cis*-manner.

Thermal decomposition

Tribenzylaluminum etherate could be heated at 230° for one h without any major decomposition. The NMR spectrum of the compound was essentially unchanged, but some toluene was collected in the cold trap.

By heating at 250° under reduced vacuum, the major product which distilled over was a 1/1 mixture of tribenzylaluminum etherate and tribenzylaluminum, as shown by the NMR spectrum. Treatment of the distillate and the distillation residue separately with deuterium oxide gave, in each case, only α-deuteriotoluene.

A solution of tribenzylaluminum etherate in mesitylene was heated at reflux for 48 h. Removal of the solvent under reduced pressure (toluene detected in the reaction solvent) and NMR examination of the residue showed the absence of any ethyl groups. The observed signals (principal singlet with shoulder at 2.15 and broad aromatic peak at 7.1) were not those of tribenzylaluminum or of its etherate. Since treatment of this residue with deuterium oxide gave only α-deuteriotoluene, it appears that structures of the type $(C_6H_5CH_2)_xAlO_y$, may have been formed.

Preparation of tribenzylaluminum (IV)

The attempted preparation of this compound by refluxing a xylene solution of dibenzylmercury with aluminum chips gave essentially only bibenzyl. The dibenzylmercury probably underwent thermal decomposition at the reaction temperature.

Satisfactory results, however, were obtained in toluene solution. A solution of 12.0 g (31.3 mmole) of dibenzylmercury (Calgon Company) and 6.0 g (0.222 g-atom) of aluminum chips (99.992 %) were heated at reflux with 100 ml of toluene for three days. The warm solution was decanted from the solid metal into another clean flask. Connection between the two flasks was maintained by a glass adapter. In this two-flask apparatus described[1] in the purification of triphenylaluminum, the crude product was crystallized twice from toluene. On each occasion the toluene solution was chilled in a solid carbon dioxide/acetone bath to cause the product to crystallize. The colorless crystals of tribenzylaluminum (7.5 g, 80%) melted at 114–116° (lit.[12] 118°). NMR (toluene-d_8): 1.48, s, 2 H; 6.67–7.17, m, 5 H.

This compound was permitted to interact, individually, with deuterium oxide, with carbon dioxide and with diphenylacetylene, using molar amounts of this substance equal to those of tribenzylaluminum etherate. Experimental conditions were the same, except where modifications are mentioned.

Treatment with deuterium oxide. This treatment yielded only α-deuteriotoluene (VI) upon work-up.

Treatment with carbon dioxide. This reaction yielded a 33% yield of *o*-toluic acid containing a trace of bibenzyl, but no trace of another acid (NMR).

Treatment with diphenylacetylene. The yield of pure 1,2,3-triphenylpropene[17] (VIII), m.p. 60–61°, was 67%. Only one product was formed.

Treatment with ultraviolet light. A solution of 1.5 g (5 mmol) of tribenzylaluminum (IV) dissolved in 150 ml of benzene was exposed to radiation of 2537 Å for 48 h. The solution was contained in a quartz vessel centered in a Rayonet Reactor, Model 100, equipped with a circular bank of low-pressure mercury lamps. After irradiation a small amount of aluminum metal had been deposited. Hydrolysis with deuterium oxide yielded toluene, which by NMR analysis was only α-deuteriotoluene. One product was separated by VPC and was shown to be bibenzyl. A second minor product or products displayed NMR peaks at 4.02, 4.35 and 7.14 ppm in a ratio of 2/4/12 and seems to be a diphenylmethane derivative.

Examination of the temperature dependence of the NMR spectrum. A dilute solution (ca. 0.05 *M*) of tribenzylaluminum (IV) in toluene-d_8 containing tetramethylsilane as an internal standard was examined at various temperatures by NMR spectroscopy. The benzyl methylene peak centered at ca. 1.48 ppm (δ-scale) changed from a very narrow, sharp signal at +25° (width at half-height, 1.5 Hz) to a broad peak at lower temperatures: −25°, 2.0 Hz; −50°, 2.5 Hz, discernible splitting; −75°, 4.5 Hz; and −90°, 9 Hz. Relative to the quintet of some toluene-d_7 centered at ca. 2.07 ppm, however, there was no significant shift in the position of the methylene group of the aluminum compound, nor were any new proton signals observed at the lower temperatures. These results are consistent with the interpretation that tribenzylaluminum is preponderantly monomeric in toluene and that $< -50°$ there is restricted rotation about the benzyl–aluminum bond. If a dimeric form of tribenzylaluminum were present in considerable amounts, one might have expected to observe bridging and non-bridging benzyl methylene signals in the NMR spectrum recorded at $< -40°$.

Treatment with benzophenone anil (X). When a yellow solution of 1.28 g (5 mmole) of benzophenone anil in 25 ml of benzene was mixed with 1.5 g (5 mmole) of the aluminum compound, an orange-colored solution was formed, possibly signifying the formation of a complex at the nitrogen atom by the Lewis acidic tribenzylaluminum. However, heating this solution at reflux for 72 h and then hydrolyzing the mixture with water gave, upon the usual work-up, almost complete recovery of unchanged benzophenone anil (97%, identified by mixture melting point).

The reaction of tribenzylaluminum (1.50 g, 5 mmole) and benzophenone anil (1.28 g, 5 mmole) was then attempted in refluxing xylene solution (15 ml). After 120 h at the reflux temperature the usual hydrolytic work-up and chromatography on a column of neutral alumina with a benzene developer yielded 65 % of the starting anil, aniline and a fraction containing ca. 20 % of triphenylethylene, 5 % of *N*-(diphenyl-*p*-tolylmethyl)aniline and 2 % of *N*-(benzyldiphenylmethyl)aniline. The identification and quantitative estimations of these compounds were achieved in the following ways: (1) the triphenylethylene was identified by its characteristic mass spectral peaks and NMR bands (in $CDCl_3$) at 6.95, 7.03 and 7.25 ppm and by brominating a sample of the reaction product (bromine in CCl_4) to yield triphenylvinyl bromide and comparing the latter with an authentic sample[23]; (2) the *N*-(diphenyl-*p*-tolylmethyl)aniline component displayed a migratory rate in TLC (on silica gel developed with pentane/ether, 50/10) that was identical with that of an authentic sample [prepared from (X) and *p*-tolyllithium][24]; furthermore, the characteristic NMR peak at 2.20 ppm confirmed its presence and permitted a quantitative estimate; (3) the *N*-(benzyldiphenylmethyl)aniline was identified and estimated by comparing its TLC and NMR behavior with that of an authentic sample[22] (NMR peak at 3.95 ppm); and (4) from the absence of characteristic NMR peaks in the crude reaction product at 5.42 (CH) and at 1.98 (CH_3) ppm, it was concluded that no significant amounts of benzhydrylaniline and *N*-(diphenyl-*o*-tolylmethyl)aniline were present.

ACKNOWLEDGEMENTS

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