

THE REACTION OF BENZYLAMINES WITH TRIALKYLALUMINUMS
UNDER IRRADIATION

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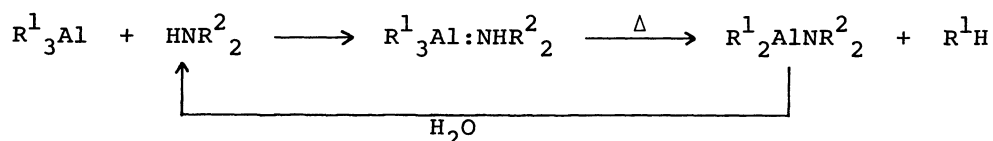
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Irradiation of benzylamines ($\text{PhCH}_2\text{NR}'\text{R}''$) complexed with tri-alkylaluminums (R_3Al) in benzene gives alkylbenzenes (PhCH_3 and PhCH_2R) and amines ($\text{HNR}'\text{R}''$). 1,2-Diphenylethane is also obtained as a side-product.

Cleavage of an amine by an organometallic compound resulting in scission of a carbon-nitrogen bond and formation of a carbon-carbon bond, has been uncommon although N,N'-benzaldipiperidine is decomposed thermally by benzylmagnesium chloride to yield N-(1,2-diphenylethyl)-piperidine in low yield.¹⁾

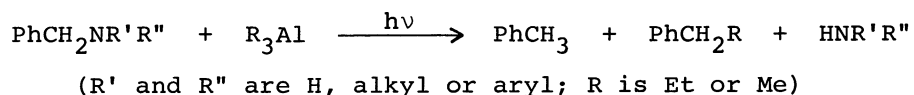
Trialkylaluminums form 1:1 complexes with primary and secondary amines, which on warming split off alkanes with formation of dialkyl-aminoaluminums. Hydrolysis of the aminoaluminums regenerates the original amines:



Donor-acceptor complexes of the type $\text{R}^1_3\text{Al}:\text{NR}^2_3$ prepared from trialkylaluminums and tertiary amines are stable thermally.²⁾ As a part of the study on the photochemical behavior of organic donors complexed with organoaluminum-acceptors,³⁻⁵⁾ we have investigated photochemical cleavage of amines in the presence of trialkylaluminums, and found that deaminoalkylation of benzylic amines takes place to form benzylalkanes together with debenzylated amines.

A benzene solution of an amine (0.10 M) and trimethylaluminum (Me_3Al) or tri-

ethylaluminum (Et_3Al) (0.13-0.14 M) in a quartz tube (sealed under nitrogen) was irradiated for ca. 50 h at a distance of 3 cm from a 300 W high-pressure mercury lamp with quartz housing. The reaction mixture was treated with aqueous alkali and the separated organic solution was analyzed by gas chromatography. The products were isolated by means of preparative gas chromatography and identified by comparison of the IR and NMR spectra with those of authentic samples. It was concluded that benzylic amines ($\text{PhCH}_2\text{NR}'\text{R}''$), whether they are primary, secondary or tertiary, react with trialkylaluminums (R_3Al) under irradiation, to form toluene (PhCH_3), benzylalkanes (PhCH_2R) and debenzylated amines ($\text{HNR}'\text{R}''$) in good to high yields. The results are summarized in Table 1.



It should be noted that the benzylic carbon-nitrogen bond of benzylamines has been reported to be in itself photosensitive.⁶⁾ Therefore, comparison was made between the reactions of N-phenethylbenzylamine and N-octylbenzylamine in the presence and absence of Et_3Al . As seen in the table, the benzylamines could in fact be decomposed photochemically at a little smaller rate than that in the presence of Et_3Al , but the reactions were complicated and the yields of phenethylamine and octylamine, respectively, were much lower, other products of unidentified structures being substantial.

A hydrogen attached to the benzylic carbon of toluene formed from the reaction of these benzylamines with added Me_3Al or Et_3Al , may not necessarily be derived from the methyl group of Me_3Al or the ethyl group of Et_3Al , since it was also obtained in comparable yields after the photolysis without the added organoaluminum. The hydrogen can presumably arise from the amino residues after breaking of the carbon-nitrogen bond of the benzylamines.

Products from cleavage of the aliphatic or aromatic carbon-nitrogen bond rather than the benzylic carbon-nitrogen bond of these benzylamines (e.g., ethylbenzene and/or butylbenzene from the reaction between N-phenethylbenzylamine and Et_3Al) were undetectable. Dicyclohexylamine was completely recovered unaltered after hydrolysis when irradiated with Et_3Al . Irradiation of diphenylamine and N,N-dimethylaniline with added Et_3Al gave traces of aniline and N-methylaniline,

Table 1.
Photochemical Cleavage of Benzylamines with Trialkylaluminums

| PhCH ₂ NR'R'' | R ₃ Al | Products (%) ^a | | |
|--|--------------------|---------------------------|---------------------|----------|
| | | PhCH ₃ | PhCH ₂ R | HNR'R'' |
| PhCH ₂ NH ₂ ^b | Et ₃ Al | 18 | 28 | <u>c</u> |
| PhCH ₂ NHMe | Et ₃ Al | 21 | 38 | <u>c</u> |
| PhCH ₂ NHMe ^d | Me ₃ Al | 42 | 39 | <u>c</u> |
| PhCH ₂ NMe ₂ | Et ₃ Al | 62 | 29 | <u>c</u> |
| PhCH ₂ NMe ₂ | Me ₃ Al | 53 | 20 | <u>c</u> |
| PhCH ₂ NHCH ₂ CH ₂ Ph ^e | Et ₃ Al | 14 | 50 | 95 |
| PhCH ₂ NHCH ₂ CH ₂ Ph ^f | ----- | 21 | -- | 7 |
| PhCH ₂ NH(CH ₂) ₇ CH ₃ ^g | Et ₃ Al | 9 | 60 | 84 |
| PhCH ₂ NH(CH ₂) ₇ CH ₃ ^h | ----- | 18 | -- | 5 |
| PhCH ₂ NHPh ⁱ | Et ₃ Al | 14 | 28 | 68 |

^a Yields are based on the amines consumed. Unless otherwise noted, conversion of the amines exceeded 90% after irradiation for ca. 50 h. In every case, 1,2-diphenylethane was obtained in 3-12% yield as a side-product. ^b 45% Conversion. ^c Not determined. ^d 44% Conversion. ^e Irradiated for 38 h; 94% conversion. ^f Irradiated for 38 h; 75% conversion. ^g Irradiated for 28 h; 93% conversion. ^h Irradiated for 28 h; 58% conversion. ⁱ Data from reference 5.

respectively, along with the substantial amounts of the recovered amines. The aliphatic or aromatic carbon-nitrogen bond of amines is thus virtually stable toward illumination even in the presence of Et₃Al. This is in sharp contrast to our previous observation that the aliphatic and aromatic carbon-oxygen bonds as well as the benzylic carbon-oxygen bond in ethers are extensively cleaved photochemically provided that they are complexed with trialkylaluminums.⁴⁾ 5,6-Dihydrophenanthridine, a cyclic benzylamine, reacted only slowly in the presence

of Et_3Al , but without any indication of formation of 2-amino-2'-methyl (and/or propyl)-diphenyl.⁷⁾

Formation of 1,2-diphenylethane in every case as a side-product may suggest that the nature of the photochemical fission of the benzylic carbon-nitrogen bond of benzylamines complexed with trialkylaluminums, is homolytic. On the other hand, diphenylmethane, an expected product from the reaction of benzyl cation or its related species with the solvent, was in no case detectable. Benzylamine or N,N-dimethylbenzylamine was stable up to 150 °C when they were heated for 50 h with Et_3Al in benzene in a sealed tube.

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- 7) Upon irradiation with ethylaluminum dichloride in benzene, however, the benzylic carbon-nitrogen bond of the cyclic amine has been shown to be easily cleaved to yield 2-amino-2'-benzyldiphenyl in nearly quantitative yield.⁵⁾

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