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Organometallic photochemistry II. Evidence for 1,1-bis(diethylalumino)ethane from the photolysis of triethylaluminum

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In Part I of this series[1], we reported that ethyllithium undergoes photolysis at 2537 Å to yield ethane, ethylene, lithium metal, and lithium hydride. In addition to β-elimination of lithium hydride, we postulated a homolytic process (Eq. 1–2) in which an ethyl radical intermediate disproportionates while still in the vicinity of the remainder of the alkyllithium aggregate. The absence of any coupling product (n-butane) was in sharp contrast to the photolysis of phenyllithium which reportedly yielded 80% biphenyl[2]. We

$$(C_2H_5Li)_6 \xrightarrow{h\nu} Li + {}^{\cdot}C_2H_5(C_2H_5Li)_5 \quad (1)$$

$$C_2H_5(C_2H_5Li)_5 \rightarrow C_2H_4 + C_2H_6 + Li + (C_2H_5Li)_4 \quad (2)$$

now wish to report that triethylaluminum can be photolyzed in the presence of mercury metal by a route which also involves reaction within the dimeric aggregate, and to offer evidence for the formation of 1,1-bis(diethylalumino)ethane in the photolytic process.

Triethylaluminum is photolyzed very slowly upon exposure to 2537 Å radiation. However, in the presence of dissolved mercury or a mercury pool, photolysis is more rapid and yields a gaseous product which consists of ethane and small quantities of butane and ethylene. In a typical run, 10 ml (0.073 mole) of neat triethylaluminum (Texas Alkyls Inc.) was irradiated for five hours in a Rayonet RP-100 reactor[1]. Standard vacuum line techniques were utilized to measure the yield of gaseous products. The results indicated that 2.14 mmoles of products were produced consisting of 97.8% ethane, 2.1% butane* and 0.1% ethylene. A colorless liquid phase remained after photolysis was terminated. Working in a dry box, this liquid was dissolved in 50 ml of dry isooctane (2,2,4-trimethylpentane), and subjected to various chemical tests. Reaction of a portion of the solution with

*Commercial triethylaluminum contains small quantities of hydride, n-butyl, and isobutyl radicals. The quantities of n- and iso-butane found in the photolysis product parallel the concentration of these groups in the starting material as determined by GLC after hydrolysis. Thus, butane was not considered to be a photolytic product of triethylaluminum.

deuterium oxide yielded a gas consisting of 99.1% ethane and 0.9% butane. Carefull mass spectrometric analysis of the ethane compared to that produced from the deuterolysis of triethylaluminum which had not been irradiated, showed the presence of 1.3% ethane-d_2 and 98.7% ethane-d_1★.

Reaction of a second aliquot with chlorine at −70° yielded ethyl chloride, butyl chloride, and 1,1-dichloroethane. No 1,2-dichloroethane was found. Analysis showed that the dichloride was produced in quantities approximately equal to that of the ethane-d_2 produced by deuterolysis. Oxidation of the photolysis product in air yielded acetaldehyde and no ethylene glycol. Other aliquots were analyzed by atomic absorption and showed no increase in mercury level after photolysis.

We interpret these results to indicate that neat triethylaluminum undergoes photolysis cleanly in the presence of mercury by an intradimer process as shown in equation 3:

$$[(C_2H_5)_3Al]_2 \xrightarrow[h\nu]{Hg} C_2H_6 + [(C_2H_5)_2Al]_2CHCH_3 \qquad (3)$$

(I)

Geminal bis-aluminum compounds such as I have been prepared previously by double addition of diethylaluminum hydride to acetylenes[3].

Photolysis of triethylaluminum/mercury in aliphatic hydrocarbon solvents results in higher yields of I. After thirty-six hours only ethane was evolved and the yield of I was determined as 10% from $C_2H_4D_2$ obtained after deuterolysis. The ethane evolved during photolysis of cyclohexane-d_{12} or benzene-d_6 solutions consists of less than 5% ethane-d_1. Thus, the intradimer process shown in Eq. 3 also apparently operates in these solutions, there being no evidence for the formation of free ethyl radicals.

It is interesting to note that the photolysis of triphenylaluminum in benzene is reported[4] to give aluminum metal and biphenyl. The photolysis of triethylaluminum in benzene yields aluminum metal and a gaseous product which consists mostly of ethane (77%) and ethylene (20%). Further work to elucidate the scope of the reaction and the role played by the mercury metal are in progress.

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★Mass spectra were determined using a high-resolution Hitachi RMU-7 spectrometer. The peak due to ions of ethane-d_2 (*m/e* 32.0595) and ethane-d_1-^{13}C (*m/e* 32.0566) from the deuterolysis of photolyzed and unphotolyzed triethylaluminum were compared under identical spectrometer conditions. A total of three runs were made to establish that the ethane-d_2 was indeed present. Because of the large amount of ethane-d_1 in the gases, we were unable to determine the position of the two deuterium atoms in the ethane-d_2.

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