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Preliminary communication

EVIDENCE FOR SINGLE ELECTRON TRANSFER IN REACTIONS OF TRIALKYLALUMINUM COMPOUNDS WITH ORGANIC SUBSTRATES

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Summary

Trialkylaluminum compounds (Me_3Al, Et_3Al and n-Bu_3Al) have been shown to react with certain ketones, alkyl halides and heterocyclic compounds to produce stable radical or radical anion-radical cation intermediates.

The degree of polar and radical character exhibited in reactions of organometallic compounds of the main group elements with organic substrates has been the subject of considerable discussion for several years. More recently, both direct evidence (EPR and CIDNP experiments) and indirect evidence (product formation studies) suggesting the involvement of single electron transfer (SET) mechanisms have accumulated for reactions of organolithium and organomagnesium compounds with organic substrates e.g., alkyl halides, ketones, polynuclear hydrocarbons, etc. [1—11]. To the best of our knowledge, there is not yet a report concerning uncatalyzed reactions of trialkylaluminum (R_3Al) compounds with ketones or alkyl halides which suggest the involvement of a SET process. In fact, some time ago we studied the addition, as well as the reduction, of benzophenone by R_3Al compounds and proposed a polar reaction pathway [12,13]. Since our recent investigations concerning the mechanisms of reaction of Grignard reagents and metal hydrides with organic substrates suggested SET processes [11,14,15], we decided to investigate a number of reactions involving R_3Al compounds. Interestingly, we have observed the involvement of SET in the reaction of R_3Al compounds (where R = Me, Et and n-Bu) with aromatic ketones (dimesityl ketone [DMK] and mesityl phenyl ketone [MPK], trityl halides (Ph_3CX; where X = Cl or Br) and heterocyclic compounds (1,10-phenanthroline and 2,2'-bipyridine). The present observations of SET are the first to be reported concerning reactions of R_3Al compounds with organic substrates.

In the present studies, we have found that when R_3Al compounds [16] (where R = Me, Et and n-Bu) were allowed to react with aromatic ketones such as DMK and MPK, deeply colored solutions were formed. In the case of Me_3Al, a light pink or violet color developed in the presence of a 10 fold excess of Me_3Al. These colored solutions are EPR active suggesting the formation of a paramagnetic species. The intensity of the EPR signal increased rapidly with time in the case of Et_3Al and n-Bu_3Al and reached a maximum beyond which the intensity decreased very slowly as the product formed. The rate of formation of the paramagnetic intermediate was found to be dependent on the nature of the trialkylaluminum compound and followed the trend: $Et_3Al >$ n-Bu_3Al $\gg Me_3Al$ [17]. The rate of formation of product followed the same trend except that Me_3Al did not produce any reduction product (no β-hydrogens). Interestingly, it appears that the rate of electron transfer is a function of the number of β-hydrogen atoms present in the alkyl group of the R_3Al compound. We have drawn a similar conclusion after studying the reactions of Grignard reagents with DMK [18].

Typically, when Et_3Al and DMK were allowed to react in THF (conc. $\cong$ 0.03 *M*) at room temperature under a dry nitrogen atmosphere, a violet color (λ_{max} $\cong$ 578 nm) appeared within a few minutes. The colored solution exhibited a complex EPR spectrum (Fig. 1) which consisted of a well-resolved hyperfine splitting pattern. Both the intensity of the EPR signal and the visible absorption increased with time in a parallel fashion and reached a maximum (concentration of radical intermediate $\geqslant$ 70% estimated by the integration of the non-modulated EPR spectrum), beyond which decay proceeded slowly resulting in the formation of reduction product. Surprisingly the product of this reaction was not the expected secondary alcohol, but rather the corresponding hydrocarbon, Mes_2CH_2. The reduction of ketones to alcohols by organometallic reagents is a well-known process. However, the reduction of ketones to hydrocarbons by organometallic reagents is most uncommon. The proposed mechanism of this reaction is outlined in Scheme 1.

It seems likely that in the present study, first the reduction of DMK to $Mes_2CHOAlEt_2$ (C) takes place via a β-hydrogen atom transfer to the dimesitylketone radical anion. Compound C then undergoes further reduction to

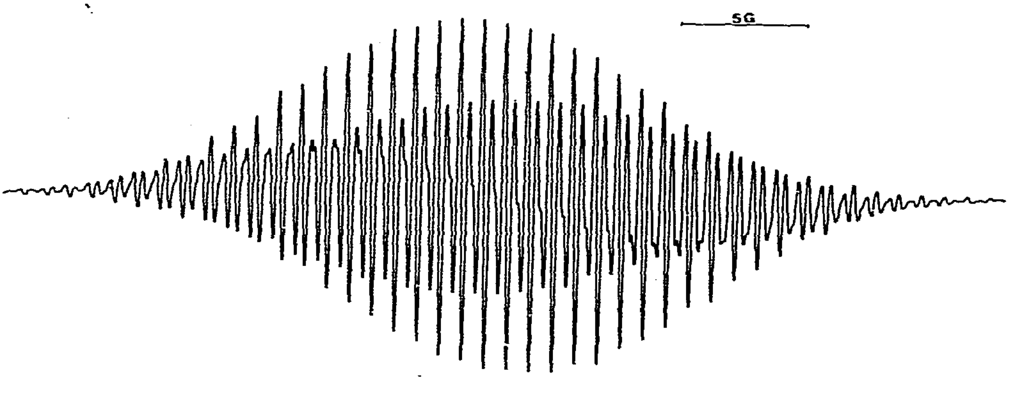
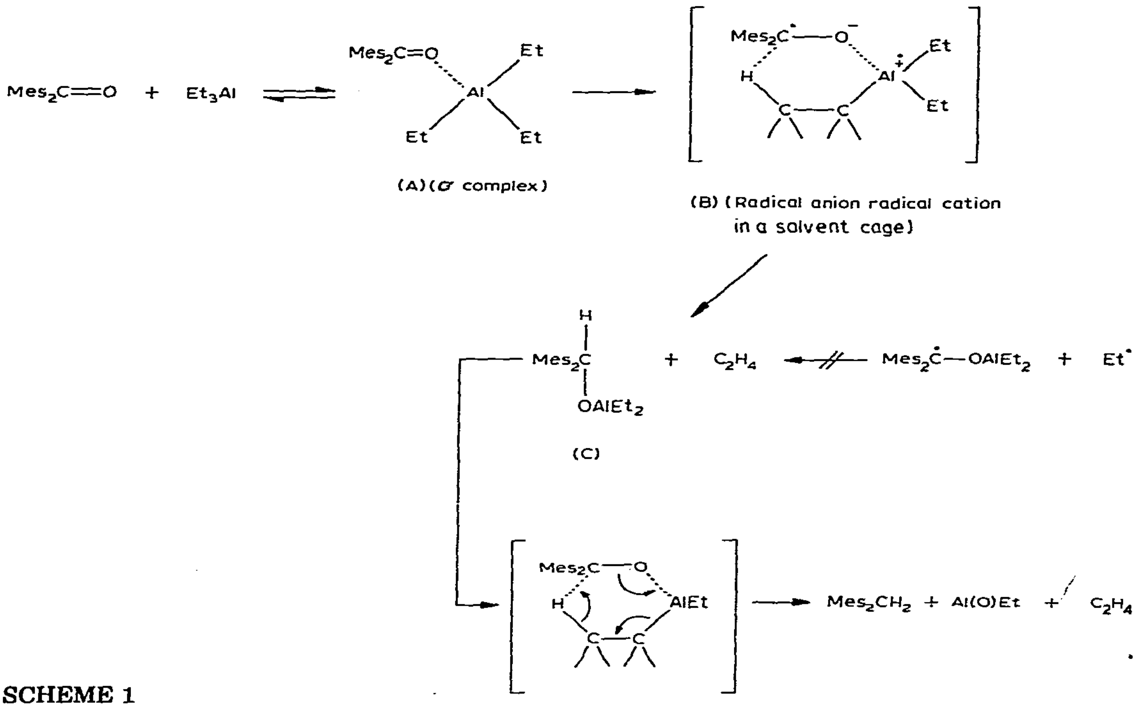


Fig. 1. EPR spectrum of Et_3Al and dimesityl ketone in THF (conc. $\cong$ 0.03 *M*) at room temperature.



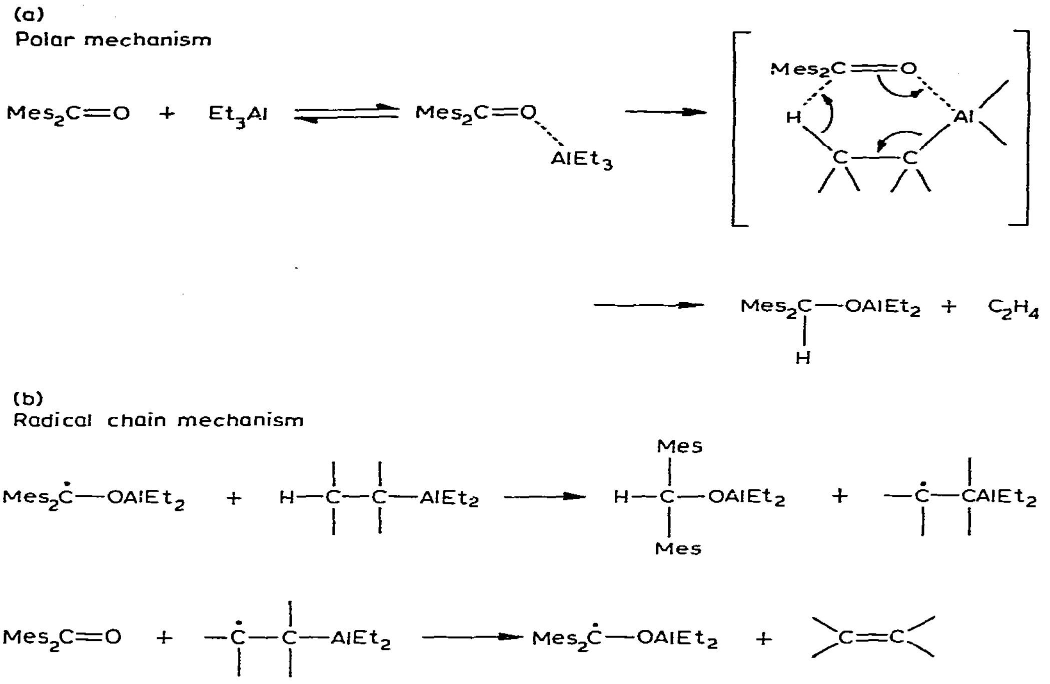
SCHEME 1

Mes_2CH_2. In order to verify this hypothesis, we prepared independently intermediate C and kept the compound in THF solution. Indeed the product (Mes_2CH_2) was found to form in this reaction with time as the solution was allowed to stand. Since high yields of reduction product were obtained in these reactions, the formation of the free ketyl ($Mes_2\dot{C}$—$OAlEt_2$) (Scheme 1) by the dissociation of the radical pair intermediate (B) is not very likely [19]. The products of the reactions of Et_3Al and $(n\text{-}Bu)_3Al$ with MPK were shown to be Mes(Ph)CH(OH) and $Mes(Ph)CH_2$ in the ratio of 7/3 after 10 days reaction time.

Other possible mechanisms are presented in Schemes 2a—2c.

The mechanisms represented by Scheme 2 can be ruled out for the following reasons: 1. a high concentration of the radical intermediate present in the reaction of Et_3Al and $n\text{-}Bu_3Al$ (as high as ≅ 70%) rules out the possibility of a polar mechanism (Scheme 2a) and the radical chain mechanism (Scheme 2b) as major reaction pathways. 2. The appearance of different EPR spectra for different reactions of R_3Al with DMK supports the presence of a radical pair (Scheme 1).

R_3Al compounds (where R = Me, Et and n-Bu) have been observed to react readily with trityl halides (Ph_3CX; where X = Cl or Br) to produce radical intermediates in every case. The radical intermediate formed in these reactions was analysed by EPR and found to be the trityl radical. The amount of radical increased rapidly with time and reached a maxium (approx. intensities ≅ 5—12%), before decreasing. The products of the reactions were found to be triphenyl methane (Ph_3CH; ≅ 20%) and the alkyl substituted product (Ph_3CR; ≅ 80%). A single electron transfer mechanism (Scheme 3) is proposed on the basis of the formation of radical intermediates.



SCHEME 2

$$\begin{tikzcd}
Ph_3CX + Et_3Al \arrow[r] & {[Ph_3CX]^- [Et_3Al]^+} \arrow[r] & {\substack{[Ph_3C + X^- + (AlEt_3)^+] \\ \text{(Solvent Cage)}}} \arrow[d, "SH"] \arrow[lld] \\
Et_2AlX + Ph_3CEt & & Ph_3CH + AlEt_2X + C_2H_4
\end{tikzcd}$$

SCHEME 3

Similarly R_3Al compounds have also been observed to react with benzhydryl halides (Ph_2CHX) via a radical intermediate to form substitution as well as reduction products.

Preliminary results involving the reactions of R_3Al compounds with heterocyclic compounds such as 1,10-phenanthroline or 2,2'-bipyridine show the formation of deeply colored solutions which have been found to be EPR active suggesting the formation of paramagnetic species. Note that this method has been used for the determination of active C—M bonds in organometallic compounds of lithium, magnesium and aluminum [21]. Work involving detailed mechanistic studies of these systems is in progress.

It is noteworthy to mention here that while the steric hindrance of DMK and MPK certainly allow the observation of an intermediate by slowing down the final step of reaction, the SET mechanism should also be applicable in reactions of other, less hindered, but equally easily reducible ketones such as benzophenone, for which no stable intermediate is observed [22].

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16 Distilled R_3Al compounds were used for the preparation of THF and benzene solutions. Solutions were standarized by NMR and aluminum analysis.
17 The over-modulated EPR spectrum of the product from R_3Al and DMK showed a singlet whereas that of MPK showed a quartet pattern. This observation is consistent with the formation of radical anions of DMK and MPK respectively. The appearance of a quartet in the case of MPK is explainable in terms of large splitting constants (≅ 4—5 G) of *ortho-* and *para*-protons of the phenyl group.
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19 Furthermore, we have recently shown [20] that dimesitylcarbinol (Mes_2CHOH) can be reduced easily to dimesitylmethane (Mes_2CH_2) by reaction of alcohol with metal hydrides (e.g., $LiAlH_4$ and AlH_3). In this reaction first an alkoxide Mes_2CHOAl is formed as an intermediate. A similar alkoxide intermediate (C) is proposed to form as the result of β-hydrogen reduction of DMK in the present studies. It appears that the conversion of Mes_2CHOAl to Mes_2CH_2 is the consequence of a rapid reaction since no additional EPR signal consisting of a large doublet expected in the case of $Mes_2CH^\bullet$ radical was observed. However, we are able to detect a trace amount of $Mes_2CH^\bullet$ radical formation in the reaction of Mes_2CHOH with $AlEt_3$ which produced the same intermediate (C) ($Mes_2CHOAlEt_2$). This suggests that if the $Mes_2CH^\bullet$ radical formed in the reaction (Scheme 1), either its concentration was so low that it was not observable in the presence of the strong signal due to the $Mes_2CO^\bullet$ radical-anion, or it rapidly goes to the product Mes_2CH_2 by coupling with hydrogen atom.
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22 This statement is based on the fact that when the reaction of benzophenone with less reactive reagents, e.g., $LiNR_2$, LiOR and LiSR which contain β-hydrogens were carried out, the reduction product (Ph_2CHOH) was observed. In all cases, formation of benzophenone radical-anion was demonstrated by EPR as the intermediate.