

## REACTIONS AND COMPLEX FORMATION BETWEEN TRIETHYL-ALUMINIUM AND METHYL METHACRYLATE

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### SUMMARY

The reaction of triethylaluminium and methyl methacrylate (MMA) was followed at room temperature in sealed NMR tubes. Hydrolysed reaction products were also analysed. Ethylation of MMA occurs only when  $\text{MMA/Al} < 1.0$ . At higher ratios a strong, unreactive 1/1 complex prevails. Evidence presented suggests that a second 1/2 complex is responsible for the reactions at lower ratios. The normal reaction is carbonyl addition: twofold carbonyl adducts of the type:  $\text{CH}_2=\text{CMeC}(\text{Et})_2\text{OAl}$ , forming rapidly. Subsequent changes appear to involve only slow exchange or association of these ethylaluminium alkoxides. Reduction of the carbonyl group occurs to a minor and irreproducible extent. There is no evidence for 1/4 attack on MMA.

### INTRODUCTION

In common with other alkyl compounds of the more electropositive metals of Groups I-III, triethylaluminium initiates polymerization of acrylate esters<sup>1,2</sup>. However there are essential differences, in that it does so only by photoinitiation<sup>1</sup> and the mechanism is a free radical one<sup>2</sup>. Nucleophilic attack on acrylate esters does occur<sup>2,3</sup> but only the products of stoichiometric addition reactions are formed: anionic polymerization chains do not develop. In conjunction with our characterization of the kinetics and mechanism of the polymerization we investigated the mechanism of the stoichiometric addition reactions and report our findings below.

### EXPERIMENTAL

Triethylaluminium (Ethyl Corporation) was drawn into a high-vacuum line under dried, oxygen-free nitrogen (which had been bubbled through an  $\text{Et}_3\text{Al}$  solution). The line was evacuated, receiving vessels flamed at ca.  $10^{-3} \text{ Nm}^{-2}$  to desorb water from the walls and the reagent distilled (at  $\leq 371^\circ\text{K}$ ). The first 70% was collected and dispensed under high-vacuum into baked glass break-seal capsules. Tests showed

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a hydride content  $< 1\%$  (by analysis of gases evolved on hydrolysis) and no ethoxide detectable by NMR. Methyl methacrylate ("Tensol cement No. 3"-ICI) was de-inhibited by alkaline washes, washed till alkali free, dried and fractionally distilled. After further drying with calcium hydride the reagent was distilled (from  $\text{CaH}_2$ ) on a high-vacuum line into baked, break-seal capsules. Solvents were similarly treated. Reference samples for gas-chromatography and mass-spectrometry were procured as follows: 2-methylpentenal by the oxidation of 2-hexanol with lead tetraacetate<sup>4</sup>; 2-methyl-2-propen-1-ol from Fluka; 3-ethyl-2-methyl-1-penten-2-ol by reaction of ethyllithium and MMA, and methyl 2-methylpentanoate by methylation of " $\alpha$ -methylvaleric acid" (K&K Laboratories).

Reactions were carried out in sealed vessels or NMR tubes, filled on a high-vacuum line in a tap-free system. Break-seal capsules were sealed to the reaction tube. After baking-out under high-vacuum, the seals were broken and the reagents run in. Once it was certain that pressure was not rising, the tube was sealed off and removed from the line.

NMR spectra were run at 60 MHz on a Varian HA-60-IL at ambient temperature using benzene as an internal lock. The amount of benzene in each tube was standardized within a series because of solvent shifts on the MMA spectrum. Reagent ratios within a tube were estimated from the ratio of the integrated  $\text{OCH}_3$  or  $\alpha\text{-CH}_3$  regions of MMA to one-third of the integrated organometallic  $\text{CH}_3$  region. Shifts are reported as  $\delta$  values relative to tetramethylsilane at  $\delta = 0.00$  ppm.

Hydrolysed reaction products were analysed on a Perkin-Elmer 800 Gas Chromatograph using 5-foot columns packed with 5% Ucon Oil LB550X on Chromosorb W at  $80^\circ$  and a Perkin-Elmer-Hitachi RMU6-D mass spectrometer. Products were isolated, where possible, using an Aerograph A 700 Preparative Gas Chromatograph using a 10-foot 20% LB550X column at  $120^\circ$ .

## RESULTS AND DISCUSSION

### (a). *Dependence of mechanism on stoichiometry*

The salient feature of the reactions between triethylaluminium and methyl methacrylate (MMA) is the sharp change in mechanism that occurs at the stoichiometry  $\text{MMA}/\text{Al} = 1.0$ . We have reported on some aspects of this change of mechanism in previous papers<sup>1-3</sup>.

When  $\text{MMA}/\text{Al} > 1.0$ , a yellow 1/1 complex (I) is formed. Under ambient illumination (or near-UV) this complex is responsible for a photoinitiated polymerization of MMA, which has been shown to be a free radical mechanism<sup>2</sup>. In the dark (or when illuminated by a red photographic safe-light) the complex is quite stable. On hydrolysis, MMA is regenerated and the volume of ethane evolved is equivalent to the number of  $\text{Et-Al}$  groups originally present. With the exception of occasional traces attributable to local triethylaluminium excesses during mixing, no products of nucleophilic attack on MMA were found, either in the dark or as concomitants of the photopolymerization.

The stoichiometry and strength of the complex (I) are demonstrated by Fig. 1 which shows the change of the internal chemical shift of the 60 MHz proton magnetic resonances of the  $\text{Et-Al}$  group as  $\text{MMA}/\text{Al}$  increases. NMR spectra of the vinyl region showed only a slight change (downfield) in the chemical shift of the vinyl protons of

MMA on the formation of the complex. The absence of strong changes suggests that it is essentially a carbonyl complex of the Wittig "ate" type.

When  $\text{MMA}/\text{Al} < 1$  several addition products could be isolated and up to 20% of the  $\text{Et}-\text{Al}$  groups were not recovered as ethane when reaction mixtures were hydrolysed after 5–10 min in the dark. The yellow colour faded as the reaction proceeded. At ratios close to  $\text{MMA}/\text{Al} = 0.5$  a sudden intensification of the colour to red was sometimes observed some minutes after mixing. The red "flash" was accompanied by sudden evolution of heat, acceleration of the reaction and the mixtures rapidly became colourless. When  $\text{MMA}/\text{Al} \leq 0.5$  the reaction was much faster than in the 0.5–1.0 range.

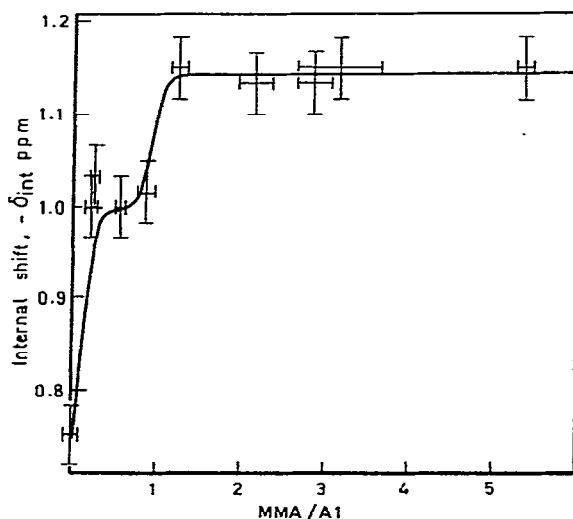


Fig. 1. Internal chemical shift of the aluminium ethyl protons:  $\delta_{\text{int}} = \delta(\text{CH}_3) - \delta(\text{CH}_2)$  ppm as a function of  $\text{MMA}/\text{Al}$  ratio. The two points where  $\text{MMA}/\text{Al} < 0.5$  refer to products, but all other points were taken when the MMA vinyl resonances were still present and the ethyl resonances retained the structure of  $\text{EtAl}$ .

Similar changes in mechanism at 1/1 stoichiometry have been observed in the reactions of trialkylaluminiums with the ketones<sup>5,6</sup>, though in these cases the change is less drastic and alkylation of the carbonyl compound does proceed, though at a reduced rate, when  $\text{R}_2\text{CO}/\text{Al} > 1$ .

Fig. 1 appears to show the presence of a second complex (II): an aluminium-rich complex, presumably with the stoichiometry  $\text{MMA}/\text{Al} = 0.5$ , though this is by no means well defined. However this is a reacting system. When  $\text{MMA}/\text{Al} < 0.5$  the reaction is fast and the points obtained in this range are those of a product not a complex. The methyl and methylene resonances have been transformed and the vinyl resonances of MMA extinguished [see (c)]. In the range  $0.5 < \text{MMA}/\text{Al} < 1.0$ , it was possible to measure the internal chemical shift while the methyl and methylene still showed the characteristic triplet-quartet pattern of  $\text{Et}_3\text{Al}$  and the MMA vinyls persisted (Fig. 2). Fig. 1 shows a slight deviation from what might be expected if the shifts over this range were governed by equilibrium between triethylaluminium and

complex (I) only. The deviation could also be due to participation of a product in the ethyl exchange equilibria (note the small, but developing product vinyl peak in Fig. 2) and so is not in itself very convincing evidence for the existence of complex (II). The hypothesis is however supported by the shifts observed in the methoxyl resonances, which suggest that MMA is complexed in a different manner when  $1.0 > \text{MMA/Al} > 0.5$  than when  $\text{MMA/Al} > 1.0$ . When  $\text{MMA/Al} > 1.0$ , only one methoxy resonance is observed and this in the same position of that in free, uncomplexed MMA. This is true even when MMA is only slightly in excess and the bulk of it must be in complex (I): *e.g.* at  $\text{MMA/Al} = 1.3$  the methoxyl resonance was at 3.42 ppm, still within experimental error of that of free MMA (note: the methoxyl and vinyl resonances are subject to a benzene solvent shift<sup>7,8</sup> and values quoted are for equivalent benzene concentration). Clearly the chemical shift in complex (I) is very similar to

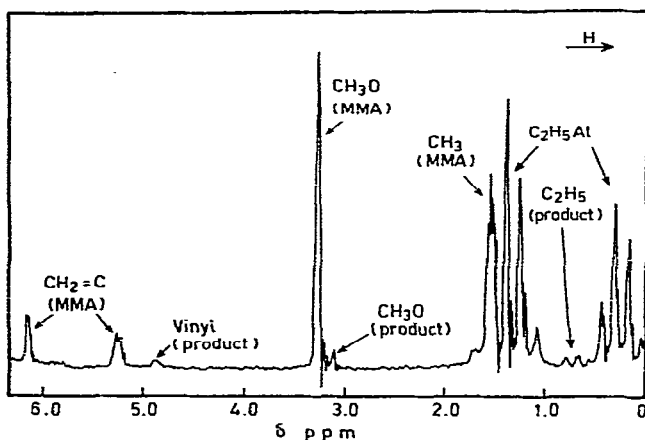
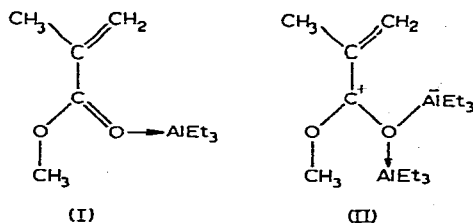


Fig. 2. 60 MHz NMR spectrum of a mixture of triethylaluminium and MMA ( $\text{MMA/Al} = 0.9$ ) some 20 min after mixing, showing the MMA vinyl peaks still intact and the triplet-quartet pattern of  $\text{Et}_3\text{Al}$ . A product vinyl peak is appearing at 4.85 ppm and a product methoxyl peak at ca. 3.08 ppm.

that in pure MMA. Between  $1.0 > \text{MMA/Al} > 0.5$  the methoxyl resonance shifts upfield; *e.g.* to 3.25 ppm at  $\text{MMA/Al} = 0.9$  (Fig. 2), which strongly suggests that a complex other than (I) is present. The precise structural reasons for the upfield shift and why it occurs with excess  $\text{Et}_3\text{Al}$  are uncertain. A complex where a second  $\text{Et}_3\text{Al}$  is coordinated to the methoxyl oxygen of MMA is structurally plausible but should lead to a downfield shift (*cf.* the 0.39 ppm downfield shift of ethyl resonances of diethyl ether in the complex  $\text{Et}_2\text{O} \cdot \text{AlEt}_3$ <sup>9</sup>). The upfield shift is most probably due to the loss of the anisotropic deshielding effect of the  $\pi$ -electrons on the carbonyl. Such a loss cannot be due to ethylation of this group (Fig. 2 shows that at this stage of reaction 90% of ethyl groups were still attached to aluminium), but it could be due to participation of the  $\pi$ -system in coordination to a second  $\text{Et}_3\text{Al}$ . If this were the case complex (I) (where the methoxyls are shielded to the same extent as in free MMA) and complex (II) might be written as:



Complex (II) must be the precursor of the nucleophilic addition products. The absence of such reactions when MMA is in excess is due to the strength of the unreactive complex (I) which at these ratios ties up all available  $\text{Et}_3\text{Al}$ .

(b). *Analysis of hydrolysed reaction mixtures (MMA/Al < 1.0)*

The reaction mixtures were hydrolysed with water and the oil and water phases separated. The aqueous phase was tested for methanol. Its presence was confirmed by the iodoform test showing that methoxyaluminium species were present in the unhydrolysed reaction products.

The non-aqueous phase on gas chromatographic analysis showed five regular products and one present on a single occasion only. The peaks were isolated on a preparative column. The products are listed in order of retention volume:

(III).  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}(\text{CH}_3)\text{CHO}$ . This could not be isolated because it overlapped the unreacted MMA peaks. It was observed as a trace on the analytical chromatograph in only one reaction mixture. Its identification rests on an identical retention volume to a test sample of 2-methyl pentanal. The reduction of esters to aldehydes by trialkylaluminiums has been reported<sup>10</sup>. It would seem probable that this aldehyde arose from the addition of a second molecule of reagent to the product of an initial reduction, though there is no conclusive evidence that the order of these two reactions was not reversed.

(IV). *An unidentified trace.* Always present.

(V).  $\text{CH}_2=\text{C}(\text{CH}_3)\text{CH}_2\text{OH}$ . The retention volume, mass spectrum and 60 MHz NMR spectrum were identical with a known sample of 2-methyl-2-propen-1-ol.

(VI).  $\text{CH}_2=\text{C}(\text{CH}_3)\text{CH}(\text{C}_2\text{H}_5)\text{OH}$ . The mass spectrum: parent peak at  $m/e = 100$ , base peak at 71 (parent ion less  $\text{C}_2\text{H}_5$ ), and prominent peaks at 85 (parent ion less  $\text{CH}_3$ ) and 41 ( $\text{C}_3\text{H}_5^+$ ), suggested 2-methyl-1-penten-3-ol. The NMR spectra, before and after the exchange of the hydroxyl with  $\text{D}_2\text{O}$ , were consistent with this assignment. These two alcohols (peaks V and VI) were always minor products. Peak V is the result of two reduction attacks on the carbonyl group and peak VI of successive reduction and alkylation.

(VII).  $\text{C}_2\text{H}_5\text{CH}_2\text{CH}(\text{CH}_3)\text{COC}_2\text{H}_5$ . Assignment based on its mass spectrum:  $m/e = 128$  (parent peak), 71 (base peak-parent ion less  $\text{C}_3\text{H}_5\text{O}$ ), 86 [McLafferty rearrangement:  $\text{CH}_3\text{CH}=\text{C}(\text{C}_2\text{H}_5)\text{OH}^+$ ], 57 (parent less  $\text{C}_5\text{H}_{11}$ ), 43 ( $\text{C}_3\text{H}_7^+$ ), 99 (parent less  $\text{C}_2\text{H}_5$ ). The McLafferty rearrangement is characteristic of a carbonyl compound. The mass spectrum suggests that it is 4-methyl-3-heptanone. It was a minor product, sometimes only present as a trace.

(VIII).  $\text{CH}_2=\text{C}(\text{CH}_3)\text{C}(\text{C}_2\text{H}_5)_2\text{OH}$ . The major product, is an isomer of peak VII showing the mass-spectrum peaks at 128 (parent), 99 (in this case the base peak),

43, 57 and 71. The McLafferty peak is absent, but a peak at 87 (parent less  $C_3H_5$ ) is third in order of intensity. The assigned structure was confirmed by its NMR spectra, before and after exchange of the hydroxyl with  $D_2O$ .

The mass spectrum of the non-aqueous phase of the hydrolysed reaction products showed no peaks above  $m/e=128$  which precludes the presence of linear and cyclic oligomers which are known to accompany anionic polymerization of MMA initiated by Grignard reagents, butyllithium, (diphenylamino)diethylaluminium and (butylthio)diethylaluminium (see ref. 3). The precursor of these oligomers:  $C_2H_5CH_2-C(CH_3)COOCH_3$ , the hydrolysed product of a 1/4 adduct, is also absent. A test sample of methyl 2-methylpentanoate had a retention time different from any gas chromatographic peak found in our reaction mixtures and its mass spectrum showed a parent peak at  $m/e=130$ , and a base peak at 88 (McLafferty rearrangement). Both were absent in the reaction products.

(c). *NMR spectra of reacting mixtures.*

When  $0.5 < MMA/Al < 1.0$ , the MMA vinyl resonances eventually disappeared and were replaced by an unresolved broad peak at  $\delta$  4.85 ppm, which is just beginning to develop in Fig. 2. At the same time the ethyl region of the spectrum became complex due to the superimposition of the back-to-front methyl-methylene pattern of  $C-C_2H_5$  resonances on the  $Al-C_2H_5$ . The methoxyl peak split, the new peak (just visible in Fig. 2) appearing 0.17 ppm upfield at  $\delta \approx 3.08$  ppm. When  $MMA/Al < 0.5$  these changes had already occurred before the spectrum could be run (Fig. 3).

The 4.85 ppm peak is very similar in shape and position to the vinyl resonance of the major hydrolysed product (VIII):  $CH_2=CMeCt_2OH$  and it is clearly a precursor having a very similar structure in the vinyl region. We believe it is the double carbonyl adduct:  $CH_2=CMeCt_2OAl$ . At reagent where carbonyl addition is rapid no further change occurred in the vinyl region of the spectrum over a period of months (Fig. 3). In these cases the integrated resonances of the vinyl region remained in a ratio of 2/3 of the methoxyl integral, showing that no significant ethylation of the vinyl group had occurred.

In two experiments, both in the range  $0.5 < MMA/Al < 1.0$ , where the ethylation is slower, long term changes did occur in the vinyl regions in the form of a new peak: a sharp singlet at 5.27 ppm. In these cases some saturation of the vinyl group had occurred, the vinyl/methoxyl integral ratios having declined to 1/2. There is no additional evidence to assist in the assignment of this peak, though a 1/4 adduct of 2-methylpropenal [a feasible, but unidentified reduction product and possible precursor of 2-methyl-1-pentanal, product (III), see (b)] is a possibility.

The methoxyl resonance always showed a long time effect (Fig. 3). The 3.08 ppm, which appears rapidly when  $MMA/Al < 0.5$  and slowly at higher ratios, also split over a period of days and was superseded by a developing peak at 3.18 ppm. Both these peaks must refer to  $Al-OCH_3$  groups. The analysis of hydrolysed reaction products showed no evidence of intermediates such as  $CH_2=CMeCt(OMe)OAlEt_2$ . The 3.08 ppm resonance was contemporaneous with the resonance in the vinyl region attributed to a doubly ethylated carbonyl group, at which stage the methoxyl group must have transferred to aluminium.

The methoxyl resonance of ethylaluminium methoxides moves upfield with increasing methoxide content. In a series of tubes prepared by the partial titration of

triethylaluminium with methanol the  $\delta$  values for  $\text{Et}_{3-x}\text{AlOMe}_x$  were: 3.34 ppm at  $x=0.34$ , 3.27 ppm at  $x=0.94$ , and 3.17 ppm at  $x=1.11$ .

When  $x < 1$  most methoxyl oxygens would be coordinated to a second Al atom, as in the cyclic trimer known to be the predominant species when  $x=1$ . When  $x > 1$ , there is an aluminium deficiency and the coordination of all alkoxy groups cannot be maintained. The upfield shift may be due to the decrease in the overall extent of coordination of methoxyls.

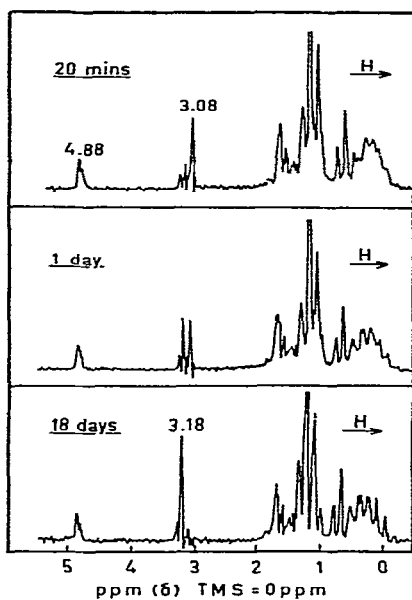
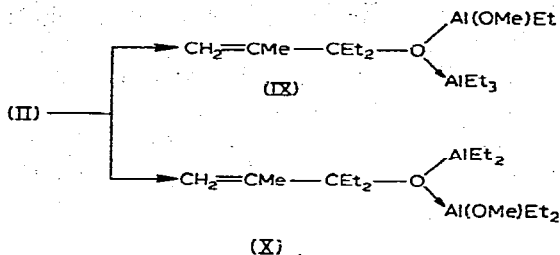


Fig. 3. Long term changes in the NMR spectrum of a mixture of  $\text{Et}_3\text{Al}$  and MMA ( $\text{MMA}/\text{Al}=0.29$ ) showing the splitting and progressive extinction of the 3.08 ppm methoxyl peak.

The time dependence of the MeO resonance of  $\text{Et}_2\text{AlOMe}$  showed a striking resemblance to that in the reacting mixtures. The original line at 3.18 ppm decreased and was replaced by one at 3.27 ppm. After 2 days the new peak was 9 times the intensity of the original, but the original did not disappear entirely, remaining as an unresolved shoulder on the upfield side of the 3.27 ppm peak 8 months later. The splitting of the MeO resonance has been reported previously<sup>11</sup> and attributed to a slow association equilibria analogous to those observed in dimethylaluminium phenoxide (several hours at room temperature<sup>11</sup>) and aluminium triisopropoxide (weeks<sup>12</sup>). It was suggested that the dimer  $\rightleftharpoons$  trimer equilibrium is the one observed.

The conditions in our reacting mixtures were not entirely analogous since we were observing species of the overall empirical formula:  $\text{Et}_{3-2x}\text{Al}(\text{OMe})_x(\text{OCEt}_2\text{-CMe}=\text{CH}_2)_x$  where  $x < 1$  ( $=0.29$  in Fig. 3). Assuming the 3.08 ppm resonance arises from the immediate product of an intramolecular reaction of complex (II), it can be attributed to either (IX), (X) or rapid exchange between (IX) and (X):



The downfield shift suggest that the 3.18 ppm peak arises from a methoxy group in which the oxygen is coordinated to another Al atom. The closely similar behaviour of the dialkyl aluminium alkoxides is strong evidence that here too a slow association is involved. However a slow exchange would also explain the observations. It is known that alkoxide groups retard the exchange of alkyls, and the larger the group the slower the exchange. With  $\text{R}_2\text{AlO-i-Bu}$  the half life for exchange of R (= Me or Et) is as long as 2 h at 313°K<sup>13</sup>.

#### CONCLUSIONS

The 1/1 complex between  $\text{Et}_3\text{Al}$  and MMA (I) is very stable and unreactive in absence of light and excess  $\text{Et}_3\text{Al}$ . When  $\text{Et}_3\text{Al}$  is in excess carbonyl addition proceeds readily. The NMR shifts when  $0.5 < \text{MMM}/\text{Al} < 1.0$  lead us to postulate that another complex (II) is present and this is the precursor of carbonyl addition. NMR evidence for such a complex is quite strong, but the rapid reaction occurring under these conditions makes it unlikely that its presence can be proved conclusively. In which case, the possibility that the addition reaction arises from the attack of uncomplexed triethylaluminium on (I) cannot be entirely excluded.

The NMR evidence suggests that carbonyl addition is normally the exclusive reaction. The exceptions were two cases where reduction of the carbonyl occurred. Only in the cases where reduction occurred did the NMR spectra show saturation of the vinyl group. Two cases of ethylation of the vinyl group were observed in hydrolysed reaction products. Product (III) arises from the alkylation of the product of an initial reduction and product (VII) most probably from the alkylation of an initial carbonyl adduct. There is no reason for supposing that 1/4 attack on MMA occurs. In the case of the normal reaction the first ethylation of the carbonyl group is quickly followed by double ethylation. There is no evidence that significant concentrations of the intermediate:  $\text{CH}_2=\text{CMeC}(\text{OEt})_2\text{O}\cdot\text{AlEt}_2$  develop.

#### ACKNOWLEDGEMENT

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