

## THE REACTION BETWEEN TRIETHYLALUMINIUM AND METHYL ISOPROPENYL KETONE

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(Received July 9th, 1970)

### SUMMARY

Triethylaluminium reacts exothermically with methyl isopropenyl ketone (3-methyl-3-buten-2-one) in hydrocarbon solution to give an intense yellow "ate"-complex, which rearranges to give the carbonyl adduct.

### INTRODUCTION

During studies on the organometal initiated polymerization of methyl isopropenyl ketone<sup>1</sup>, the reaction between triethylaluminium and methyl isopropenyl ketone in hydrocarbon solution at room temperature was investigated. Baba<sup>2</sup> recently studied the reaction between triethylaluminium and various  $\alpha,\beta$ -unsaturated carbonyl compounds, but there are no reports in the literature for the reaction with  $\beta$ -unsubstituted  $\alpha,\beta$ -unsaturated ketones.

### EXPERIMENTAL

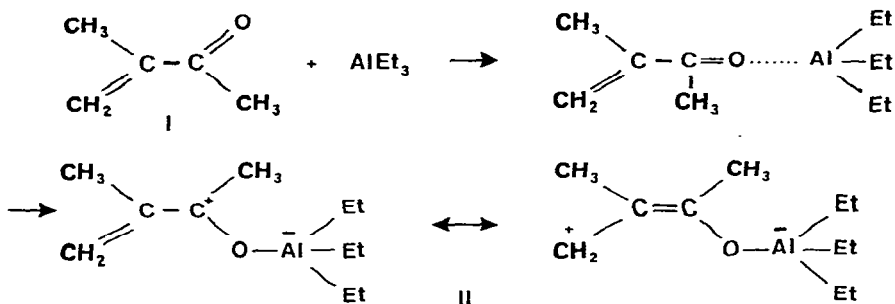
Triethylaluminium (Koch-Light) was distilled under high vacuum and made up gravimetrically into solutions of the required concentration in dry nitrogen filled vessels, sealed with serum caps.

Methyl isopropenyl ketone, prepared, dried and purified as previously described<sup>3</sup>, was shown (VPC Perkin-Elmer F11, DE301 Carbowax column, 160°) to be at least 99.9% pure. It was made up to the required concentrations as above. Toluene (A.R.) and benzene (A.R.) were dried and fractionated as described elsewhere<sup>3</sup>. Cyclohexane (Spectrosol) was dried over sodium wire and used without further purification. Mixtures for spectroscopic studies were prepared, using hypodermic syringes, as described for triethylaluminium. UV and IR spectra were recorded on Unicam SP800B and SP200 instruments respectively. NMR spectra were measured on a Varian A60.

### RESULTS AND DISCUSSION

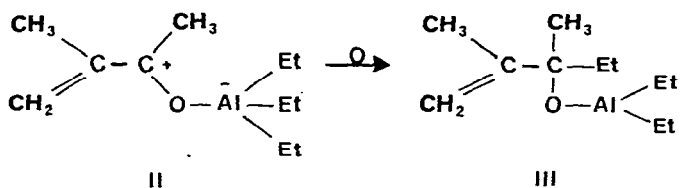
The exothermic addition of methyl isopropenyl ketone (I) to triethylaluminium

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in toluene, benzene and cyclohexane gives rise to an intense yellow. This colour is associated with the production of the conjugated "ate"-complex or "betain" (II)<sup>4</sup>.

The yellow fades, rapidly at first, due to the rearrangement of the betain to products. Spectroscopic studies of various molar ratios of methyl isopropenyl ketone and triethylaluminium show that a 1/1 reaction occurs. NMR shows no significant loss of the vinyl protons ( $\tau$  4.45, 4.59) although the chemical shifts are modified ( $\tau$  4.98). IR shows that at 1/1 molar ratios the carbonyl frequency ( $1670\text{ cm}^{-1}$ ) is removed, whereas the carbon-carbon double bond ( $1640\text{ cm}^{-1}$ ) is retained. The non-production of gaseous products, under high vacuum conditions<sup>1</sup>, indicates that the reduction and enolization reactions are negligible. The major product of the reaction at room temperature is therefore the 1/1 carbonyl adduct (III).



With excess triethylaluminium the spectra obtained are the summation of the 1/1 carbonyl adduct and the excess organometal; the solutions rapidly become colourless. With excess methyl isopropenyl ketone, the intense yellow fades to a pale straw, which is maintained throughout the subsequent polymerization reaction. The reaction mixture becomes heterogeneous as white poly(methyl isopropenyl ketone) is produced.

#### ACKNOWLEDGEMENTS

The authors wish to thank Professor M. C. R. Symons, University of Leicester, for helpful discussions.

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