

## Preliminary communication

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### Alkoxy donation of ester group to organoaluminium compound

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#### SUMMARY

A novel type of coordination, involving bonding to aluminium of the alkoxy atom of an ester group, has been observed in the products formed from  $\beta$ -carbomethoxypropionaldehyde and organoaluminium compounds.

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During an investigation of the polymerization of polar-substituted aldehydes<sup>1</sup>, the addition and coordination reaction of  $\beta$ -carbomethoxypropionaldehyde  $\text{CH}_3\text{OC}(\text{O})\text{CH}_2\text{CH}_2\text{CH}=\text{O}$  (I) with trimethyl- and triethylaluminium was studied. The reactions between (I) and organoaluminium in 1/1 and 1/2 molar ratios were carried out at 0° in an atmosphere of nitrogen in methylene chloride or benzene.

The addition compound was isolated by distillation only for the 1/1 product from trimethylaluminium (II). The distillate (b.p. 40°/1 mmHg) was collected in a glass ampoule which was cooled below -50° and sealed in vacuo. It had a freezing point of  $-63 \pm 1^\circ$  and decomposed readily at room temperature, but was stable in solution. The molecular weight determined cryoscopically in benzene was 168 ( $\text{C}_8\text{H}_{17}\text{O}_3\text{Al}$  calcd. 188). The infrared spectrum (10% solution in methylene chloride) showed absorptions at 1775, 1195, 1165, 1050 and 940  $\text{cm}^{-1}$ . The NMR signals (10% solution in methylene chloride) appeared at  $\tau$  10.78 (singlet, 6H), 8.65 (doublet, 3H), 8.2 (multiplet, 1H), 7.7 (multiplet, 1H), 7.5 (multiplet, 2H), 6.50 (singlet, 3H), and 5.4 (multiplet, 1H). [The chemical shifts were measured relative to  $\text{CH}_2\text{Cl}_2$  ( $\tau$  4.70).]

The appearance of methine proton signal at  $\tau$  5.4 and methyl proton signal at  $\tau$  8.65 indicates that the aldehyde group had reacted with trimethylaluminium to give a Grignard-type addition product. It is interesting to note that the ester-carbonyl frequency appeared at 1775  $\text{cm}^{-1}$ , showing a high frequency shift of 35  $\text{cm}^{-1}$  relative to that of (I), which is at 1740  $\text{cm}^{-1}$ . This absorption shifted to 1690  $\text{cm}^{-1}$  in the 1/2 reaction product, but returned to 1775  $\text{cm}^{-1}$  by the further addition of I. The shift to 1775  $\text{cm}^{-1}$  was also

observed for both 1/1 and 1/2 reaction products with triethylaluminium (the latter product showed no shift to a lower wave number).

The shift of the carbonyl absorption band to a higher frequency is most unusual,

but can be interpreted in terms of alkoxy donation,  $\begin{matrix} \text{Al} \\ \uparrow \\ \text{---C---O---} \\ \uparrow \\ \text{C=O} \end{matrix}$ . Such coordination is also

indicated by an unusual upfield chemical shift of the methoxy proton from  $\tau$  6.33 in (I) to 6.50 in (II). Molecular weight measurement indicates that (II) is monomeric. The coordination probably occurs intramolecularly to satisfy the valence of aluminium, and the structure proposed for (II) is shown in Fig. 1. The methylene protons adjacent to the asymmetric carbon attached to methyl group exhibited two separate and distinct NMR signals at  $\tau$  8.2 and 7.7, the difference between these is comparable to those between axial and equatorial protons in cycloalkane derivatives, and this provides additional evidence for ring formation.

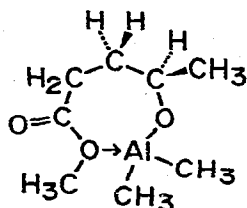


Fig. 1. The structure of the addition compound of  $\beta$ -carbomethoxypropionaldehyde with trimethylaluminium (II).

It is noteworthy that the alkoxy donation occurs in preference to carbonyl donation, which would also form a seven-membered ring. The alkoxy group is presumably more favourably placed to interact with the oriented vacant orbital of the aluminium atom.

Hydrolysis of (II) with an excess of water and subsequent extraction with methylene chloride gave  $\gamma$ -valerolactone in a 75% yield instead of the expected hydroxy-ester compound. It is assumed that ring closure of the hydroxy-ester compound occurs because of a stereochemical effect similar to that which gives rise to alkoxy donation in (II)<sup>2</sup>.

#### REFERENCES

- 1 H. Sumitomo, K. Kobayashi and T. Saji, *J. Polym. Sci., Part A-1*, 10 (1972) in press.
- 2 H.B. Henbest and B.J. Lovell, *J. Chem. Soc.*, (1957) 1965.