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Preliminary communication

A novel 1,3-shift of an organoaluminium group: NMR studies of $Me_2Al(RNCO)OMe$

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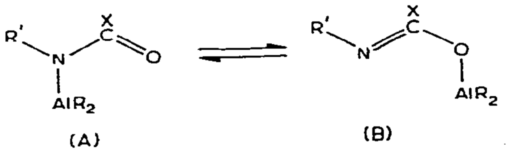
The relationship between the structure and the reactivity of $R_2Al(R'NCO)X$ compounds was discussed in our previous papers[1,2]. Structure A, containing the Al–N bond, which is relatively reactive towards R'NCO is presumed to be predominant in the case of X = NMe_2, whereas with X = OMe, structure B, involving the unreactive Al–O bond is dominant.



1,3-shifts of organometallic groups from the N-atom to the O-atom were confirmed by NMR studies in the case of Group IVB organometallics such as carbamates or acid amides[3]. In this communication, the hitherto unconfirmed 1,3-shift of the organoaluminium group has been demonstrated by study of the NMR spectra of $Me_2AlN(C_6H_5)CO_2Me$ from +20° to –87°C.

As a model compound, the white crystalline dimethylaluminium derivative of methyl *N*-phenyl carbamate was prepared in good yield by treatment of $(C_6H_5)NHCO_2Me$ with Me_3Al, m.p. 95–97°C (Anal.: Found: C, 57.61; H, 6.65; Al, 13.87%. $C_{10}H_{14}AlNO_2$ calcd.: C, 57.97; H, 6.81; Al, 13.03%.). The compound was dimeric in the benzene solution as indicated by cryoscopic measurement.

Its NMR spectra in toluene solution were measured in the range of +20° to –87°C, the results are shown in Fig. 1.

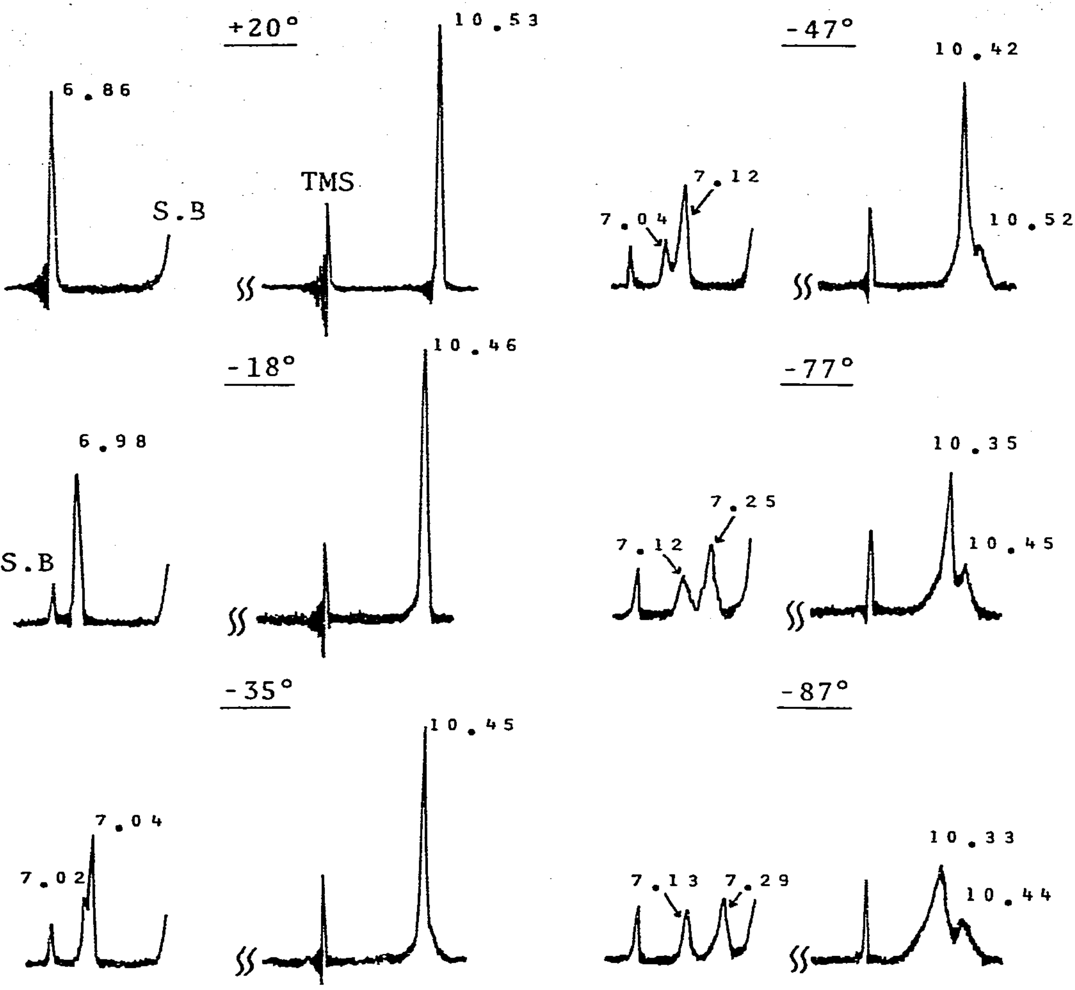


Fig.1. NMR spectra of $Me_2Al(PhNCO)OMe$ at various temperatures (in toluene). (S.B. means the spinning side band of toluene.)

The coalescence behaviour of the Me_2Al and MeO groups was thermally reversible. Although the coalescence temperatures of both $AlMe_2$ and OMe appear to differ from each other, they may in fact be the same.

The observed splitting can be ascribed to the freezing of the structures of the species, A and B.

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