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A. M. CAPORUSSO, G. GIACOMELLI, L. LARDICCI (\*)

## ON THE REACTION OF TRI-ISOBUTYLALUMINIUM WITH PIVALONITRILE

**Summary** — The reaction of pivalonitrile with  $\text{Bu}_3^i\text{Al}$  was investigated under a variety of conditions. The nitrile was reduced with low conversions, which increased however operating in the excess of the organoaluminium compound: no addition to the carbon-nitrogen triple bond was detected, contrary to what previously observed in the reaction of  $\text{Bu}_3^i\text{Al}$  with  $\text{PhCN}$ .

The overall results are discussed and possible mechanisms for the reaction are suggested.

Investigations on the dynamics of the reaction between  $\text{Bu}_3^i\text{Al}$  (I) and  $\text{PhCN}$  have been carried out in connexion with studies on the reactivity of simple functional substrates towards  $\beta$ -branched organometallic compounds and on their possible synthetic applications (GIACOMELLI and LARDICCI [1972; 1973], LARDICCI and GIACOMELLI [1971], LARDICCI et al. [1974]).

In order to gain further informations about the influence of the nature of the nitrile on the reactivity of  $\text{Bu}_3^i\text{Al}$  (I) we have investigated the reaction (1) using  $\text{Bu}^t\text{CN}$  (II) as a model of aliphatic substrate.



All the experiments were carried out according to procedures already described (LARDICCI and GIACOMELLI [1971]), in the absence

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(\*) Istituto di Chimica Organica, Facoltà di Scienze M.F.N. dell'Università di Pisa. Centro di Studio del C.N.R. per le Macromolecole Stereordinate ed Otticamente Attive.

of solvents, in the range of temperatures 66.5-86.5°C, and at various molar ratios of the reactants.

Pivalonitrile (**II**) reacts with compounds (**I**) at a very reduced rate (Table): at  $[I]/[II] = 1$ , conversions higher than 30 per cent are obtained only after 6h at 86.5°C (run 3). The presence of an excess of compound (**I**) in the reaction mixture ( $[I]/[II] \geq 2$ ) results in an appreciable increase of the conversions yet at 66.5°C (runs 4,8). Contrary to what observed with PhCN (LARDICCI and GIACOMELLI [1971]) and in agreement with results previously obtained in the reaction of  $Et_3Al$  with  $Bu^tCN$  (JENNINGS et al. [1965]), the reaction (**1**) yields only the reduction product (**III**) despite of the experimental conditions adopted (Table).

TABLE  
Reaction of tri-isobutylaluminium (*I*) with pivalonitrile (*II*)

Run	$[I]/[II]$	temp. (°C)	(III) (mole per cent) a), b)
1	1.0	66.5	4
2	1.0	76.5	13
3	1.0	86.5	32
4	2.0	66.5	25
5 c)	2.0	66.5	11
6	2.0	76.5	74
7	2.0	86.5	100
8	4.0	66.5	69

a) Reaction time: 6h; b) determined by g.l.c. analyses of the reaction mixtures after hydrolysis; c) reaction carried out with tri-isobutylaluminium diethyl etherate.

Like PhCN, at  $[I]/[II] = 1$ ,  $Bu^tCN$  should be reduced *via* the formation of a  $Bu_3^iAl-Bu^tCN$  coordination adduct (**IV**) followed by the thermal migration of the  $\beta$ -hydrogen from the isobutyl group of compound (**I**) to the nitrile carbon atom (GIACOMELLI and LARDICCI [1973], LARDICCI and GIACOMELLI [1971]).

The change in the optical rotation of a toluene solution of (+)-tris-[(S)-2-methylbutyl]-aluminium as a function of the concentration of compound (**II**) (Figure) indicate effectively the presence of a  $Bu^tCN-AlR_3$  adduct whose formation is very fast and quantitative. The fact that the thermal rearrangement of the adduct (**IV**) occurs slowly and leads only to the reduction product (**III**) might be related to the steric hindrance of the *t*.butyl group. From this

point of view the migration of the bulky isobutyl group, bound to the aluminium atom, should be prevented and that of the  $\beta$ -hydrogen atom should be hindered. The reduced reactivity of the adduct (IV) respect to that of  $\text{PhCN-AlBu}_3^i$  adduct should very likely depend on the electronic factors too <sup>(1)</sup>.

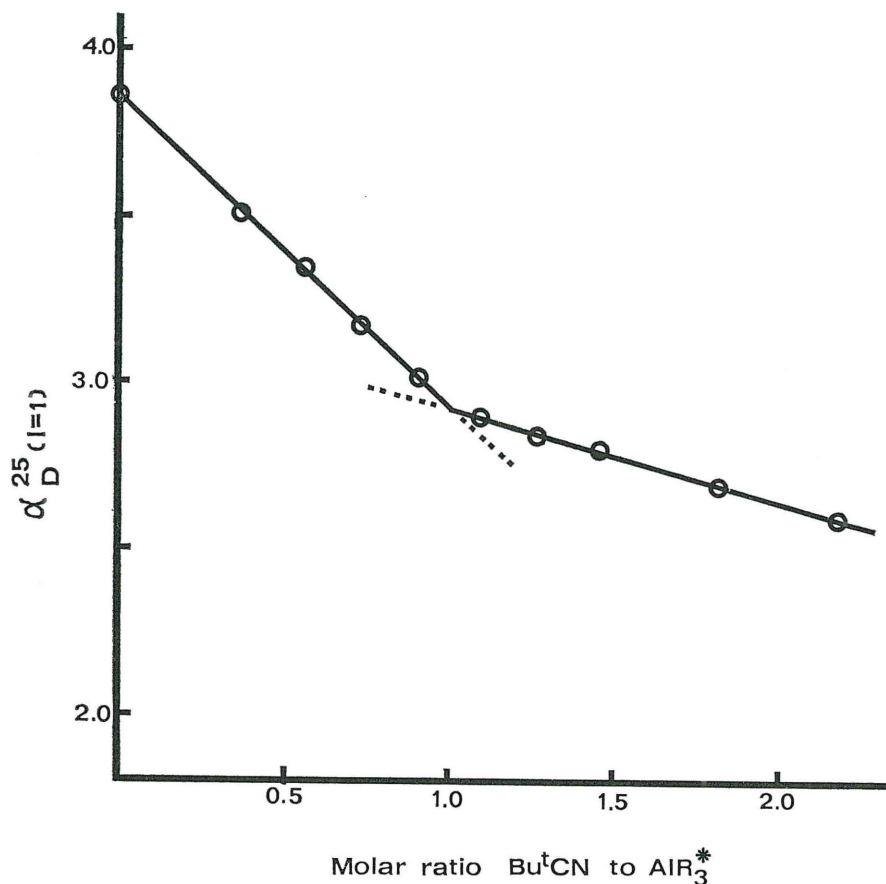
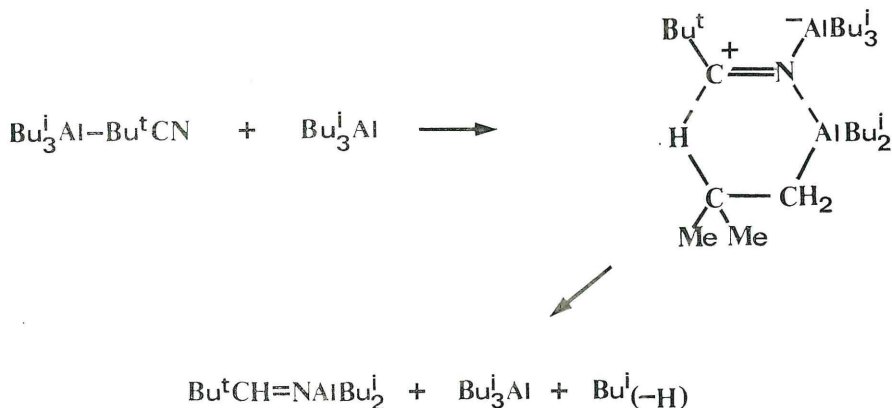


Figure - Complex formation between tris[(S)-2-methylbutyl]-aluminium and pivalonitrile in toluene.

(1) N.m.r. spectra at 60 MHz in the absence of solvents showed that the complexation of compound (I) with the nitriles causes an upfield shift of the resonance lines of the protons  $\alpha$  to the aluminium atom, this shift being greater in the case of  $\text{Bu}^t\text{CN-AlBu}_3^i$  adduct (0.50 p.p.m.) than in that of  $\text{PhCN-AlBu}_3^i$  adduct (0.31 p.p.m.). These results might be consistent with the different electron-releasing ability of the two nitriles.

Regard to the results obtained in the presence of an excess of  $\text{Bu}_3^i\text{Al}$  ( $[\text{I}]/[\text{II}] \geq 2$ ), the intervention of  $\text{Bu}_2^i\text{AlH}$  [from thermal decomposition of compound (I)] does not explain completely the increased reduction rate, at least at  $66.5^\circ\text{C}$ ; in fact, on the basis of the rate of formation of  $\text{Bu}_2^i\text{AlH}$  at  $66.5^\circ\text{C}$  (LEHMKUHL and ZIEGLER [1970]), the contribution of hydride species to the reduction does not exceed 4 per cent. Furthermore, the reduction rate is raised respect to that observed when the reaction is carried out at molar ratio of 1 even if the adduct (IV) is treated with an equimolecular amount of triisobutylaluminium diethyl etherate (run 5) which does not form the aluminium monohydride even at temperatures of  $100^\circ\text{C}$  (PAIARO and BALDI [1961]). Therefore the relatively higher conversions observed (Table) might be better rationalized supposing that the uncomplexed compound (I) reacts with the adduct (IV) in a six-membered cyclic transition state.



As above assumed for the thermal rearrangement of the adduct (IV), the steric hindrance to the nitrile carbon atom of compound (II) should prevent the migration of the isobutyl group bound to the aluminium atom.



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