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INSERTION REACTIONS OF DIETHYLALUMINIUM DERIVATIVES
V. REACTIONS OF DIETHYLALUMINIUM ALKOXIDES WITH PHENYL ISOCYANATE

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SUMMARY

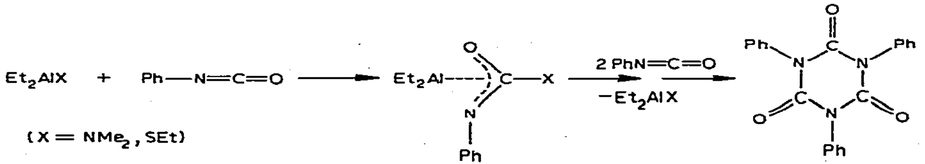
Reaction of phenyl isocyanate and diethylaluminium alkoxide, Et_2AlOR (R = Me, Et, i-Pr, t-Bu and benzyl) in equimolar or 3/1 molar ratios gave mainly diethylaluminium derivatives of *N*-phenyl carbamate esters, in contrast to the corresponding reactions with Et_2AlNMe_2 or Et_2AlSEt.

The diethylaluminium allophanate, $[PhN(AlEt_2)CONPhCO_2R]$, was found to be unstable, readily decomposing to the carbamate and isocyanate.

INTRODUCTION

Phenyl isocyanate acts as a typical acceptor in addition reactions[1] with Group IVb organometallic compounds, $\geq$M–X, (M = Si, Ge, Sn, and X = NR_2, OR, SR, PR_2).

In a previous paper[2], the reactions of Et_2AlNMe_2 or Et_2AlSEt with isocyanates were shown to proceed with Al–N or Al–S bond cleavage to give 1/1 adducts as well as the cyclic trimer (isocyanurate).



(1)

Few papers have been published dealing with the reaction behavior of Et_2-AlOEt compounds. Those available indicate that (a) reaction between β-propiolactone and Et_2AlOEt at 70° for 24 h leads to the formation of diethylaluminium 2-(ethoxycarbonyl)ethanolate as a result of acyl–oxygen bond cleavage[3], and (b) in the presence of Et_2AlOEt as a catalyst an alternating copolymerization reaction occurs between phenyl isocyanate and ethylene oxide, as reported by Harada *et al.*[4].

No detailed study has however been reported to date on the reactions of phenyl isocyanate and various diethylaluminium alkoxides.

RESULTS AND DISCUSSION

Reactions of phenyl isocyanate and five kinds of diethylaluminium alkoxide, $\mathrm{Et_2AlOR}$ (R = Me, Et, i-Pr, t-Bu and benzyl), were carried out in equimolar or 3/1 molar ratios in benzene solution initially at $-5°$, the temperature being gradually raised to reflux over a period of 5 h. Isolation of the 1/1 adduct formed was not however possible because the equilibrium mixture between the 1/1 adduct and starting materials showed a tendency to revert completely to the starting materials even at room temperature in benzene solution. For this reason, the reaction products were hydrolysed with aqueous ethanol containing hydrochloric acid, the yields of the hydrolysis products (carbamate, allophanate, isocyanurate and sym-diphenyl urea) being tabulated in Table 1.

TABLE 1

YIELD OF REACTION PRODUCTS OF PhNCO AND VARIOUS $\mathrm{Et_2AlOR}$ COMPOUNDS

R	Ratio Al/PhNCO	Products, yield (%)[a]			
		$\mathrm{PhNHCO_2R}$	$\mathrm{H(NPhCO)_2OR}$	$\mathrm{(PhNCO)_3}$	$\mathrm{(PhNH)_2CO}$
Me	1/1	29	6	7	14
	1/3	22	17	31	11
Et	1/1	51	6	10	9
	1/3	30	11	14	13
i-Pr	1/1	46	8	11	13
	1/3	31	10	13	18
t-Bu	1/1	11	3	8	25
	1/3	19	4	7	20
$\mathrm{CH_2Ph}$	1/1	50	7	trace	10
	1/3	25	13	22	11

[a] Expressed as a percentage of isocyanate unit incorporated in each product relative to that present initially.

The use of a 3/1 molar reaction mixture did not markedly affect the yields of hydrolysis products obtained in comparison to those obtained with equimolar reactants. The main product among the hydrolysis products was the carbamate (except in the case of t-BuNCO) in reactions involving both 1/1 and 3/1 molar reactant ratios, suggesting that the further insertion of isocyanate groups into the product is difficult which is completely contrary to observations during the reaction of phenyl isocyanate with $\mathrm{Et_2AlNMe_2}$ or $\mathrm{Et_2AlSEt}$[2]. In the latter cases, the use of a 3/1 molar ratio of reactants gave the cyclic isocyanate trimer as the principal product of the reaction.

From the results shown in Table 1, the relative reactivity order of $\mathrm{Et_2AlOR}$ appears to be: R = benzyl $\gtrsim$ ethyl > isopropyl $\gtrsim$ methyl > tert-butyl, which is similar to the order found in the exchange reaction[5].

As described above, the pure 1/1 adduct from the reaction between phenyl isocyanate and various alkoxides $\mathrm{Et_2AlOR}$ could not be isolated, and in an attempt to overcome this problem the preparation of $\mathrm{R_2Al(NR'CO)OMe}$ by reaction of an equimolar mixture of methyl carbamate $\mathrm{R'NHCO_2Me}$ and $\mathrm{R_3Al}$ in toluene solution was attempted. Three new pure compounds, $\mathrm{Me_2AlNPhCO_2Me}$ (92% yield),

TABLE 2

DATA RELATING TO $R_2AlNR'CO_2Me$

R	R′	M.p. (°)	n^a	Analysis found (calcd.) (%)			Chemical shifts [τ(ppm)]			
				C	H	Al	HCAl	HCCAl	HCO	HCN
Me	Me	73–76	1.90	41.21 (41.38)	8.17 (8.33)		10.45		6.73	7.45
Me	Ph	95–97	1.88	57.61 (57.97)	6.65 (6.81)	13.87 (13.03)	10.45		6.85	
Et	Ph	77–79		61.62 (61.11)	7.68 (7.71)	12.13 (11.47)	9.81	8.75	6.81	

[a] Degree of association in ca. 2.5% benzene soln. determined cryoscopically.

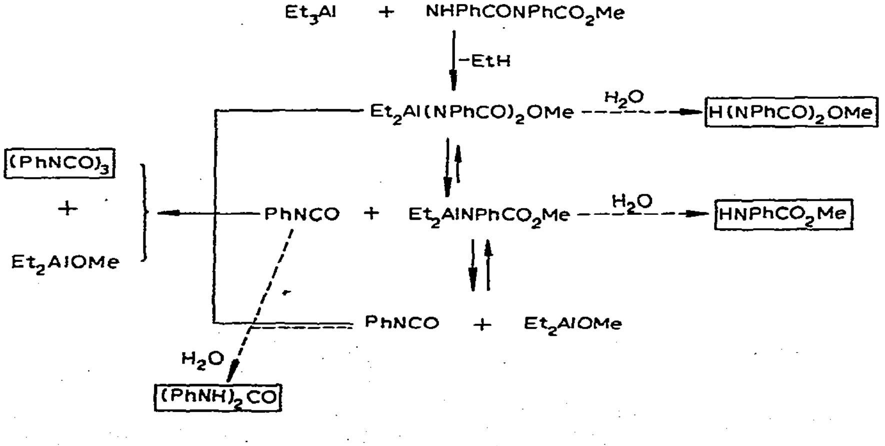
$Me_2AlNMeCO_2Me$ (69%) and $Et_2AlNPhCO_2Me$ (96%) were obtained, and their melting points, elemental analyses, NMR spectral details and degrees of association are shown in Table 2.

These crystalline compounds were relatively stable. In benzene solution, however, conversion to a mixture of the decomposition products (R_2AlOMe, R′NCO) occurred after a few hours even at room temperature. Hydrolysis under acidic condition gave the corresponding carbamate in high yield, along with small amounts of $(PhNH)_2CO$.

$Et_2AlNPhCO_2Me$ was allowed to react with equimolar amounts of PhNCO in toluene at room temperature for 72 h, but only 9.5% of phenyl isocyanurate (based on PhNCO as the starting unit) was obtained.

In an attempt to prepare the methyl diethylaluminium-substituted allophanate, *i.e.*, the 2/1 adduct of phenyl isocyanate with Et_2AlOMe, methyl-*N*,*N*′-diphenyl allophanate was allowed to react with Et_3Al in toluene solution at $-5^\circ \sim +20^\circ$ for 24 h. After complete evolution of ethane the resulting mixture exhibited IR absorptions at 2260, 1735, 1710 and 1695 cm^{-1}, indicating decomposition of the 2/1 adduct,

SCHEME 1



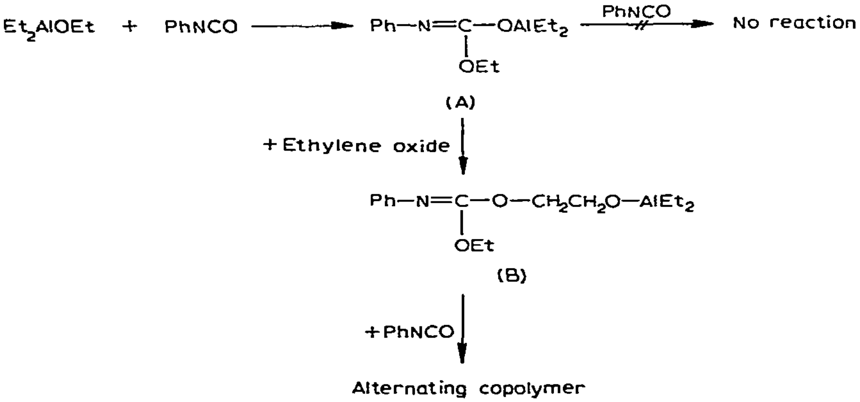
the hydrolysis products being $(PhNH)_2CO$, $PhNHCO_2Me$, $PhNHCONPhCO_2Me$ and $(PHNCO)_3$ in 24, 45, 16 and 5% yield, respectively.

From this it follows that $Et_2AlNPhCONPhCO_2Me$ is very unstable and decomposes readily into the Et_2Al-substituted carbamate and phenyl isocyanate, as shown in the Scheme 1.

This scheme also offers an explanation for the course of the reaction between Et_2AlOR and excess PhNCO since the product distribution in that reaction is also similar.

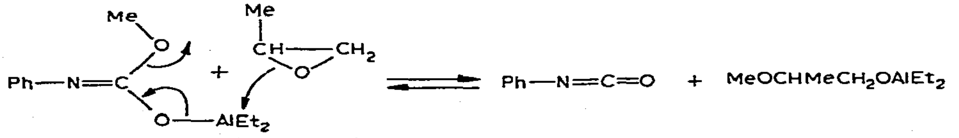
In order to compare the relative reactivity of Al–N and Al–O bonds, $Et_2AlNMeCH_2CH_2OAlEt_2$ (b.p. 111–116°/0.05 mm, 64% yield) was prepared from the reaction between Et_3Al and 2-(methylamino)ethanol in benzene solution. Hydrolysis of the reaction product from an equimolar mixture of PhNCO and the above *N,O*-bis(diethylaluminium) compound gave mainly $PhNHCONMeCH_2CH_2OH$, indicating that Al–N bonding to the isocyanate is stronger than the corresponding Al–O bonding.

Harada *et al.*[4] have described an alternating copolymerization reaction between phenyl isocyanate and ethylene oxide, catalyzed by Et_2AlOEt. They explained the copolymerization reaction as follows. [eqn. (2)]



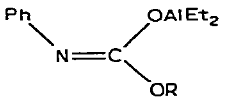
(2)

In this scheme, structure (B) has a similar structure to Et_2AlOEt and is capable of reacting with an isocyanate molecule. In our experiments however, reaction of an equimolar mixture of propylene oxide and $Et_2AlNPhCO_2Me$ led to the elimination of phenyl isocyanate as depicted in eqn. (3).

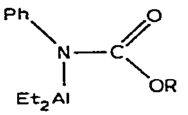


(3)

It is reasonable to suggest that the insertion product has a structure similar to that of (C) (which is similar to that of (A) put forward by Harada) rather than that of its isomer (D).

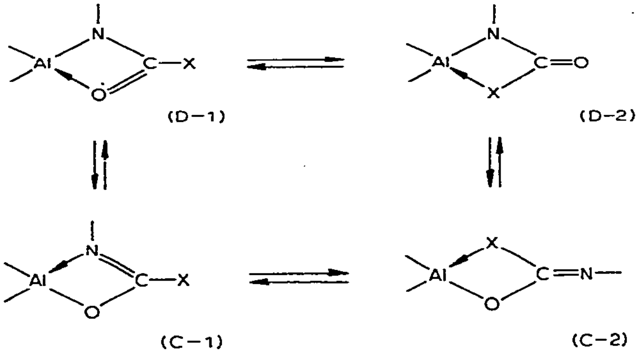


(C)



(D)

The suggestion that the low reactivity of the Al–O bond inhibits the subsequent insertion of PhNCO is consistent with the observed result. An equilibrium cycle similar to that in eqn. (4), in which isomers of structures (C) and (D) are included, would explain the behavior of the 1/1 insertion products.



(4)

In the reaction with Et_2AlNMe_2, structure (D) containing the active Al–N bond would be the major species involved in subsequent reaction with another PhNCO molecule.

The Et_2Al group would also be capable of a 1,3-shift in these equilibria, and in order to obtain clearer evidence, NMR studies at various temperatures, especially at low temperature, are now in progress[6].

EXPERIMENTAL

Preparation of diethylaluminium alkoxides and general procedures

Diethylaluminium alkoxides, Et_2AlOR (R = Me, b.p. 56–58°/0.3 mm; R = Et b.p. 61–63°/0.3 mm; R = i-Pr, b.p. 82–85°/0.2 mm; R = t-Bu, m.p. 143–145°; R = benzyl, b.p. 135–139°/0.1 mm) were prepared from Et_3Al and the corresponding alcohols and purified by distillation or sublimation. The degree of association based on the cryoscopic molecular weight was nearly 2 in each case except methoxide in which it was 3. NMR peaks of $(CH_3CH_2)_2Al$ protons usually appeared at τ 8.71 ~ 8.76 (CH_3, triplet) and 9.86 ~ 9.90 (CH_2, quartet).

Hydrocarbon solvents were dried with Na-wire and CaH_2. All reactions were carried out under dry nitrogen. NMR, IR spectra and elemental analyses were undertaken as described previously[2].

Reactions of Et_2AlOR and PhNCO (in various molar ratios)

Diethylaluminium alkoxide, Et_2AlOR (about 10 mmoles) in 10 ml benzene solution was allowed to react with either an equimolar or a 3-times molar amount of phenyl isocyanate in 10 (or 15) ml benzene solution at −5°, the temperature being gradually raised to reflux during a period of 45 h. The reaction mixture was cooled and hydrolyzed at room temperature with aqueous ethanol ($H_2O/EtOH = 9/1$) containing several drops of conc. HCl. The resulting colloidal precipitates were removed and the aqueous fraction extracted with ether and then with chloroform. The following treatment in the case of the methoxide is typical. When the ether extract was cooled, a precipitate of $(PhNH)_2CO$, m.p. 238–240°, was obtained in 14% yield based on the amount of phenyl isocyanate used. After removal of $(PhNH)_2CO$ and ether, the viscous liquid residue was distilled under reduced pressure to recover PhNCO (in trace, in the cold trap), $PhNHCO_2Me$ (m.p. 46–47°) and the second residue, which was analyzed spectroscopically and found to be a mixture of $PhNHCO_2Me$ (1710 cm^{-1}) and $PhNHCONPhCO_2Me$ (1730 cm^{-1}). Yields of carbamate and allophanate of 29% and 6%, based on the amount of starting PhNCO, were obtained.

The values of the yields obtained by spectroscopic analysis were practically identical with those obtained using column chromatography on Kieselgel (70–325 mesh) and developed with chloroform. From the chloroform extract, the cyclic trimeric isocyanate, m.p. 283–285°, was obtained in 7% yield. Yields of the hydrolyzed products obtained in the reactions of PhNCO and Et_2AlOR in molar ratio 1/1 or 3/1 have already been summarized in Table 1.

Preparation of the compounds $R_2Al(NR'CO)OMe$ ($R = Me, Et$; $R' = Me, Ph$) and their reactions

An attempt to isolate pure $R_2Al(NR'CO)OMe$ from the reaction mixture prepared as above was unsuccessful despite careful treatment and manipulation.

Me_3Al (2.88 g, 40 mmoles) in 5 ml toluene (not benzene) was added to an equimolar amount of $NHPhCO_2Me$ (m.p. 46–48°) in 3 ml toluene at temperatures between −10 and −5°. After quantitative evolution of methane, the solvent was removed under reduced pressure at room temperature. The resulting white crystalline needles were further dried *in vacuo* to give pure $Me_2Al(NPhCO)OMe$ in 92% yield. Two analogous compounds were similarly prepared and their physical data are given in Table 2.

The reaction of $Et_2Al(NPhCO)OMe$ with an equimolar amount of propylene oxide in benzene gave free PhNCO and $Et_2Al[OCH_2CH(OMe)CH_3]$.

Reaction of methyl (N,N'-diphenyl)allophanate with Et_3Al

$PhNHCONPhCO_2Me$ (3.20 g, 12 mmoles) was treated with an equimolar amount of Et_3Al in 20 ml toluene at temperatures between −5 and +20° for 24 h. After complete evolution of ethane the resulting mixture exhibited IR absorptions at 2260, 1735, 1710 and 1695 cm^{-1}. Subsequent hydrolysis gave $(PhNH)_2CO$, $PhNHCO_2Me$, $PhNHCONPhCO_2Me$ and $(PhNCO)_3$ in 24, 45, 16 and 5% yield, respectively.

$PhNHCONPhCO_2Me$ was prepared quantitatively from *N,N'*-diphenyl-1,3-diazetidine-2,4-dione (cyclic dimer of phenyl isocyanate) and methanol using Bu_3SnOMe as a catalyst.

Synthesis of $Et_2AlOCH_2CH_2NMeAlEt_2$ and its reaction with PhNCO

2-(Methylamino)ethanol (3.95 g, 50 mmoles) in 10 ml benzene was slowly added to a twice molar amount of Et_3Al (11.4 g) in 20 ml benzene solution at −5° and the temperature raised to reflux. After ethane evolution (184% based on aminoalcohol), removal of solvent following distillation gave a fraction of b.p. 111–116°/0.05 mm, 7.39 g (64%), which was identified as $Et_2AlOCH_2CH_2NMeAlEt_2$ by the two characteristic kinds of $AlCH_2CH_3$ signal, NMe signal (τ 7.85) and peaks at τ 6.42 ($-OCH_2$, t), 7.70 ($-NCH_2$, t) in its NMR spectrum.

PhNCO (1.02 g, 8.7 mmoles) was carefully added to 10 ml of a benzene solution of 2-(diethylalumoxy)-*N*-(diethylaluminium)-*N*-methylethylamine (2.10 g, 8.6 mmoles) under similar conditions to those used with Et_2AlOEt and the mixture hydrolyzed to give a viscous liquid which consisted mainly of $PhNHCONMeCH_2CH_2OH$ as verified by the following spectroscopic data: NMR, NMe (τ 7.26, singlet); IR, ν(OH) 3300 cm^{-1}, ν(C=O) 1690 cm^{-1} (urea carbonyl group and not carbamate group).

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