Journal of Organometallic Chemistry, 284 (1985) 1–4
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

REACTION OF DIETHYLHYDROXYBORANE WITH TRIALKYLALUMINIUM

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(Received September 18th, 1984)

Summary

The reaction of diethylhydroxyborane with trialkylaluminium has been studied. Trialkylboranes and diethyltriisobutyldialuminium dioxide were isolated and characterized. A two-stage mechanism is proposed for the formation.

Introduction

In the reaction of water with trialkylaluminium, dialkylhydroxyaluminium, R_2AlOH, was proposed as the intermediate [1] (eq. 1):

$$H_2O + 2R_3Al \xrightarrow{-RH} R_2AlOH \cdot R_3Al \rightarrow R_2AlOAlR_2 \qquad (1)$$

Due to its stability, diethylhydroxyborane was presumed to provide a good model for obtaining diethylboryldialkylaluminium oxide (I) similar to aluminoxane (eq. 2):

$$Et_2BOH + R_3Al \xrightarrow{-RH} \underset{(I)}{[Et_2BOAlR_2]} \qquad (2)$$

The analogous compounds were proposed as intermediates in the reactions of boric oxide with organoaluminium compounds (Et_2AlCl, $Et_3Al_2Cl_3$, $EtAlCl_2$) [2] (eq. 3):

$$B_2O_3 + R_2AlCl \rightarrow [>BOAl<] \rightarrow R_3B + >AlOAl< \qquad (3)$$

Köster and Serwatowski obtained a dimeric diethylboryldichloroaluminium oxide in the reaction of tetraethyldiboroxane with aluminium chloride [3] (eq. 4):

$$Et_2BOBEt_2 + AlCl_3 \xrightarrow{-Et_2BCl} 1/2(Et_2BOAlCl_2)_2 \qquad (4)$$

An investigation of $>BOAl<$ systems was undertaken with the view of obtaining a better understanding of the chemistry of aluminoxanes, the structures of which are still the subject of discussion [4].

0022-328X/85/$03.30

Results and discussion

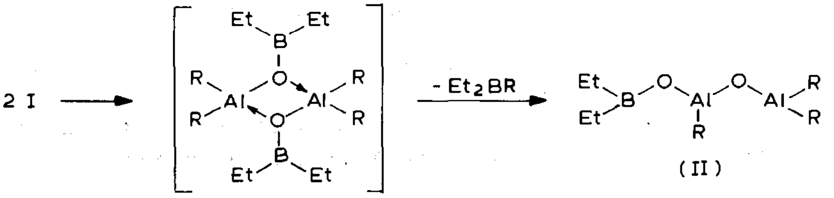
The reaction of diethylhydroxyborane with trimethylaluminium, as well as with triethylaluminium, in aliphatic and aromatic hydrocarbons took place at −90°C, accompanied by considerable evolution of methane or ethane. The reaction of diethylhydroxyborane with triisobutylaluminium was carried out at room temperature, using benzene as a solvent; in this case, isobutane was evolved.

The reaction of diethylhydroxyborane with trialkyl-aluminium proceeds in two stages. During the first stage (eq. 2) the evolution of aliphatic hydrocarbon and the formation of the unstable diethylboryldialkylaluminium oxide (I) take place. Attempts to isolate this oxide by distillation yielded a volatile liquid fraction.

The ^{1}H NMR spectrum of the distillate was identical, in the case of trimethyl- and triethylaluminium, to that of diethylmethylborane and triethylborane, respectively [5], with the solvent signals excluded. A white, amorphous solid residue, oxidizing easily in the presence of air, was found to be insoluble in aliphatic and aromatic hydrocarbons. In this product the molar ratio of boron to aluminium was always less than one, although the substrates were introduced according to the stoichiometry of reaction 2, i.e. $Et_2BOH/R_3Al = 1/1$.

In the case of triisobutylaluminium, the ^{1}H NMR spectrum of the distillate was difficult to elucidate. The multiplet (τ 7.65 ppm) and the overlapping doublets (τ 8.98 and 9.00 ppm) were respectively ascribed to the methine, methyl and methylene protons present in the isobutyl group of diethylisobutylborane. Other signals (in the range of 8.6–8.9 ppm) probably derived from the protons of the boron-bound ethyl groups. After the volatile components were distilled off, a thick, sticky, colourless liquid, soluble in benzene and toluene, was obtained wherein the molar ratio of boron to aluminium was 1/2, although the substrates were introduced according to the stoichiometry of reaction 2, i.e. $Et_2BOH/(i\text{-}Bu)_3Al = 1/1$. In the ^{1}H NMR spectrum of the product, the multiplet (τ 7.72 ppm) and doublets (τ 8.86 and 9.62 ppm) ascribed to the methine, methyl and methylene protons of the aluminium-bound isobutyl groups, respectively, were present. Other signals (in the range of 8.9–9.0 ppm) probably derived from the protons of the boron-bound ethyl groups. Within the range characteristic for M–O–M moieties, the IR spectrum of the product comprised two absorption bands of high intensity that were not observed in the spectra of the substrates. The band in the range 760–820 cm^{-1} was ascribed to the stretching vibrations of the Al–O–Al moiety while the band in the range 640–670 cm^{-1} was attributed to the stretching vibrations of the B–O–Al moiety. The latter band overlapped the Al–C valence vibrations [1]. The molecular weight of the product corresponded to the molecular weight of dimeric diethylboryltriisobutyldialuminium dioxide (found: 608; calculated for $Et_2BO_2Al_2(i\text{-}Bu)_3$: 326).

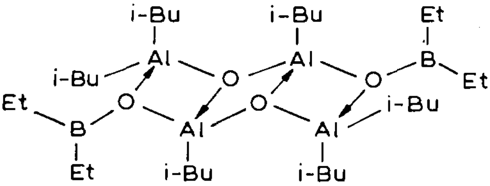
These phenomena may be explained assuming that in the second stage oxide I undergoes a polycondensation reaction to form oxide II, which has a boron to aluminium molar ratio less than one:



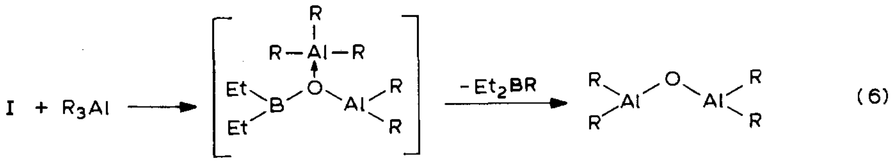
(5)

Depending on the reaction conditions and the type of aluminium-bound alkyl substituent, oxide II may undergo further condensation to form an oxide of the formula $Et_2B(OAlR)_nOAlR_2$, in which the molar ratio of boron to aluminium is still lower, and evolving trialkylborane thereby. The condensation reaction is facilitated by a high reaction temperature, a high initial concentration of the trialkylaluminium compound, and a low alkyl substituent bound to the aluminium atom. It proceeds even in diethyl ether, thus proving that this electron donor does not stabilize the unstable [$>$B–O–Al$<$] moiety.

The stability of the diethylboryltriisobutyldialuminium dioxide is probably due to steric hindrance preventing the rearrangement of isobutyl group from aluminium to boron atom in the dimeric oxide (II):



If the reaction of diethylhydroxyborane with a trialkylaluminium compound is carried out at room temperature, then the possibility of formation of diethylalkylborane in the subsequent reaction of oxide I with trialkylaluminium cannot be excluded (eq. 6):



It seems, however, that the complete rearrangement of trialkylaluminium, which, as confirmed by the quantitative evolution of methane or ethane, respectively, takes place at −90°C when reaction 6 is harly probable, and the absence of aluminium in the distillate indicate that condensation reaction 5 is primarily responsible for the formation of diethylalkylborane.

The alkyl exchange between diethylhydroxyborane and trialkylaluminium [6] does not seem to play an important role in the first stage of the process. In all cases, the alkane corresponding to the aluminium-bound alkyl substituent is exclusively obtained (eq. 2).

Experimental

The reactions of diethylhydroxyborane with trialkylaluminium compounds were carried out using hydrocarbons and diethyl ether as solvent, at various temperatures. To a cooled solution of trialkylaluminium, ca. 20% (by weight) solution of diethylhydroxyborane was added dropwise, under vigorous stirring. After the evolution of gas had ceased the reaction mixture was left to reach room temperature. The solvent and diethylalkylborane were distilled off in vacuo leaving diethylborylalkylaluminium oxide as the residue. The distillate and oxide were analysed and the contents of

TABLE 1

CONDITIONS OF THE REACTION OF DIETHYLHYDROXYBORANE WITH TRIALKYLALUMINIUM AND THE COMPOSITION OF THE OXIDE OBTAINED

Reaction temperature (°C)	Concentration of R_3Al (% by weight)	Solvent	Molar ratio of B/Al/R(Al)
With trimethylaluminium			
−90	14.7	toluene	1/3/4
−90	4.4	toluene	1/2/3
20	4.4	benzene	1/5.5/7.5
−70	4.9	diethyl ether	1/2/3
With triethylaluminium			
−90	2.3	toluene	1/2/3
0	4.5	pentane	1/2.4/2.2
20	5.4	pentane	1/4/6.8
With triisobutylaluminium			
20	7.2	benzene	1/2

boron, aluminium and aluminium-bound alkyl groups were determined (Table 1) [7].

Diethylhydroxyborane was obtained according to the method described by Köster et al. [8].

^{1}H NMR spectra were recorded on a JEOL JNM-100 MHz spectrometer. IR spectra were recorded on a Zeiss UR-10 spectrometer in a KBr cell. The molecular weight was determined by cryoscopic measurements in 5.75% (by weight) benzene solution.

Acknowledgements

The authors thank Drs. J. Florjańczyk, K.B. Starowieyski and A. Okniński for helpful discussions and the Institute of Heavy Organic Synthesis "Blachownia" for financing the research.

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