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A NEW OXIDATION PROCEDURE FOR ORGANOALUMINUM COMPOUNDS * [1]

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Summary

Organoaluminum compounds are conveniently oxidized by trimethylamine *N*-oxide. The corresponding alcohols are obtained in nearly quantitative yields. Triphenylaluminum is oxidized readily using the new procedure but vinyl moieties appear to be unaffected.

Introduction

Organoaluminum reagents [2] are important synthetic intermediates both in the laboratory and in commercial applications. The oxidation of alkylaluminum compounds, followed by hydrolysis to give the corresponding alcohols, is carried out on a multimillion pound per year scale industrially (eq. 1).

$$R_3Al \xrightarrow{O_2} (RO)_3Al \xrightarrow{H_3O^+} 3\ ROH \qquad (1)$$

Product yields from oxidation by molecular oxygen are reported to appraoch 100% [3] but are often in the 70—90% range [4]. These oxidations presumably proceed via a free radical chain process analogous to the oxidations of other organometallic compounds [5—7]. Formation of peroxides, hydrocarbons, and hydrogen during these oxidations support a mechanism involving radicals [5,8].

We recently concluded a study which demonstrated that trimethylamine *N*-oxide and the corresponding hydrate were convenient oxidizing agents for organoboranes [9—11]. We wish to report that trimethylamine *N*-oxide is also a convenient reagent for the oxidation of organoaluminum reagents (eq. 2).

$$R_3Al \xrightarrow[\Delta]{3(CH_3)_3NO} (RO)_{32}Al \xrightarrow{H_3O^+} 3\ ROH \qquad (2)$$

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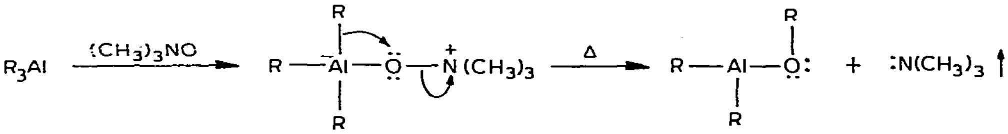
* Dedicated to Professor Herbert C. Brown for his contribution to chemistry.

Results and discussion

The reaction of trimethylamine *N*-oxide with organoaluminum reagents was first reported by Köster [12]. The reaction produces a 1/1 addition complex which is stable at room temperature. We have found that this complex rearranges readily at higher temperatures to yield the corresponding alkoxy derivative (eq. 3). Further reaction produces the totally oxidized derivative which yields the alcohol upon hydrolysis (eq. 4). The results are summarized in Table 1.



$$R_3Al \xrightarrow{(CH_3)_3NO} R-\underset{R}{\overset{R}{\overset{-}{Al}}}-\ddot{O}-\overset{+}{N}(CH_3)_3 \xrightarrow{\Delta} R-\underset{R}{\overset{R}{Al}}-\ddot{O}: + :N(CH_3)_3\uparrow \qquad (3)$$

$$R_2AlOR \xrightarrow[\Delta]{2(CH_3)_3NO} (RO)_3Al \xrightarrow{H_3O^+} 3\ ROH \qquad (4)$$

The oxidation is temperature dependent. The rate increases with increasing temperature. The results for tri-n-propylaluminum, which are representative, are shown in Fig. 1.

The oxidations of a variety of primary alkylaluminum compounds proceed at nearly the same rate under comparable conditions. The only exception is trimethylaluminum which is oxidized rather slowly. The dimeric nature of this compound, even at elevated temperatures, presumably retards formation of the necessary amine *N*-oxide complex [13]. The results are summarized in Fig. 2.

Products and yields of the oxidation reactions of organoaluminum reagents with $(CH_3)_3NO$ are summarized in Table 1.

Not surprisingly, oxidation of mixed tri-n-alkylaluminum reagents proceeds in a statistical fashion. Thus the oxidation of isobutyldi-n-decylaluminum with

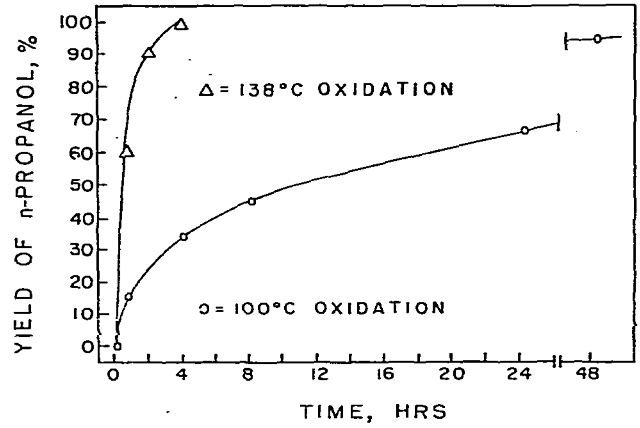


Fig. 1. Temperature effects on the oxidation of tri-n-propylaluminum.

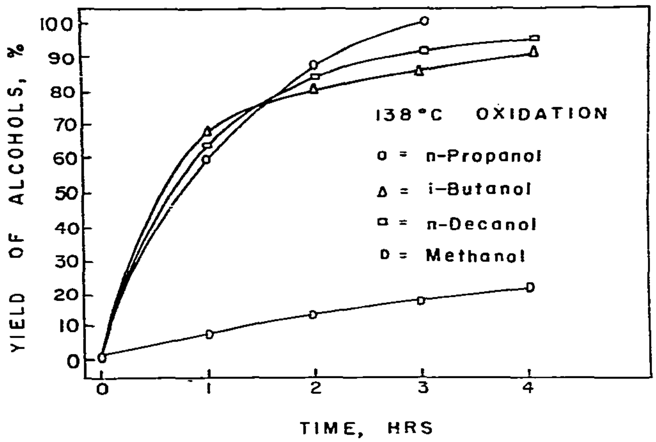


Fig. 2. Relative rates of oxidation of various trialkylaluminum reagents.

one equivalent of trimethylamine *N*-oxide produces an equivalent of alcohols in a 2/1 ratio (n-decanol: isobutanol).

The trimethylamine *N*-oxide procedure is unique in that triphenylaluminum is oxidized rapidly to generate phenol. Oxidation of arylaluminum compounds utilizing molecular oxygen is reported to be slow and inefficient (eq. 5) [14].

$$Ph_3Al \xrightarrow[\Delta]{(CH_3)_3NO} \xrightarrow{H_2O} 3\ PhOH \qquad (5)$$

Surprisingly, vinyl groups are not oxidized by the reagent. Reaction of vinyldialkylaluminum reagents with trimethylamine *N*-oxide affords oxidation of only the alkyl portion of the reagent *.

Reactions of alkylaluminum dihalides, dialkylaluminum halides and alkylaluminum sesquihalides with trimethylamine *N*-oxide produce only tars under the conditions utilized.

Experimental

Proton NMR spectra were recorded on a Varian Associates T-60 spectrometer, The yields for the oxidation of the aliphatic organoaluminum compounds were determined via NMR. Gas chromatographic analyses were performed on a

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* No aldehyde products were observed during the oxidations of diisobutyl(1-hexenyl)aluminum and diisobutyl(2-phenylethenyl)aluminum; after hydrolysis, 1-hexene and styrene, respectively, were present in significant amounts (in addition to isobutanol). The reaction is complicated by the condensation [15] of the vinyl groups during the reaction period. As an example, NMR analysis of a hydrolyzed aliquot of the reaction mixture containing diisobutyl(2-phenylethynyl)aluminum and trimethylamine *N*-oxide at the point where 40% of the isobutyl groups had been oxidized revealed the presence of styrene (~50% of the theoretical amount), 1.3-diphenyl-1-butene [16] (the condensation product), and polystyrene; no phenylacetaldehyde was detected. At completion of the reaction (100% yield of isobutanol), hydrolysis yielded, no styrene and no phenylacetaldehyde but a major amount of 1,3-diphenyl-1-butene (accounting for ~70% of the original vinyl groups) and polystyrene.

TABLE 1

OXIDATION OF ORGANOALUMINUM REAGENTS WITH $(CH_3)_3NO$

Reagent	Product	Yield (%) [a]
Trimethylaluminum	Methanol	21
Tri-n-propylaluminum	n-Propanol	100
Triisobutylaluminum	Isobutanol	94
Tri-n-octylaluminum	n-Octanol	94
Tri-n-decylaluminum	n-Decanol	94
Triphenylaluminum	Phenol	97 [b]
Diisobutyl(2-phenylethenyl)aluminum	Isobutanol	100 [c]
Diisobutyl(1-hexenyl)aluminum	Isobutanol	100
Diethylaluminum chloride	Ethanol	0
Ethylaluminum dichloride	Ethanol	0
Ethylaluminum sesquichloride	Ethanol	0

[a] Yields determined by NMR after 4 h at 138°C. [b] Yield determined by GLC after 1 h at 138°C. [c] Yield determined by NMR after 3 days at 80°C.

Varian Aerograph 90-P equipped with a 1.5 m × 7 mm column packed with 15% SE-30 on Chromosorb P 60—80. The yield of phenol was determined by GLC.

Materials. Trimethylamine *N*-oxide was prepared by subliming the commercially available (Aldrich) trimethylamine *N*-oxide dihydrate. The sublimed amine *N*-oxide was transferred in a dry glove bag and stored under dry Argon until used. Triisobutylaluminum and diisobutylaluminum chloride were used as received from Texas Alkyls. Trimethylaluminum, tri-n-propylaluminum, diisobutylaluminum chloride, diethylaluminum chloride and ethylaluminum dichloride were used as received from Ventron Corporation. Diisobutylaluminum hydride was used as the neat liquid which was obtained by distillation of a pentane solution (Ventron.) *m*-Xylene was dried over molecular sieves prior to use.

Preparation of organoaluminum compounds. (a) Tri-n-octylaluminum: 1-octene (30 mmol, 4.69 ml) and diisobutylaluminum hydride (10 mmol, 1.42 g) were added to a dry, nitrogen-flushed, 50-ml flask fitted with a sidearm, reflux condenser, mercury bubbler and magnetic stirrer. The reaction mixture was heated to 110°C (oil bath) and stirred at this temperature for two days to insure complete conversion to tri-n-octylaluminum. (b) Tri-n-decylaluminum: tri-n-decylaluminum was prepared in a manner analogous to tri-n-octylaluminum. 1-Decene (30 mmol, 5.66 ml) was used and the reaction mixture was heated to 140°C. (c) Diisobutyl(1-hexenyl)aluminum: *m*-xylene (15 ml) and 1-hexyne (10 mmol, 1.15 ml) were added to the apparatus described above. The flask was cooled to 0°C and diisobutylaluminum hydride (10 mmol, 1.42 g) was added. The reaction mixture was allowed to warm to room temperature while stirring overnight. (d) Diisobutyl(2-phenylethenyl)aluminum: The reagent was prepared in a fashion analogous to diisobutyl(1-hexenyl)aluminum utilizing phenylacetylene (5 mmol, 0.55 ml) and diisobutylaluminum hydride (5 mmol, 0.71 g). (e) Triphenylaluminum: triphenylaluminum was prepared from triphenylborane and trimethylaluminum according to a published procedure [17].

Oxidation of the organoaluminum compounds. The oxidation of tri-n-propylaluminum is representative. The tri-n-propylaluminum (10 mmol, 1.56 g) and *m*-xylene (15 ml) were added via syringe to the equipment described above. While flushing the flask with nitrogen, the reflux condenser was removed and anhydrous trimethylamine *N*-oxide (30 mmol, 2.25 g) was added in one portion. With the reflux condenser attached, the reaction flask was placed in an oil bath (140°C). The reaction mixture was gently refluxed with efficient stirring for 4 h. Aliquots were removed at 1 h intervals and analyzed by proton NMR to determine the extent of oxidation.

Isolation of products. The water insoluble alcohols were isolated as follows. The reaction mixture was cooled to room temperature and 25 ml 6 *N* HCl was slowly added. The contents of the reaction flask were transferred to a separatory funnel. The flask was rinsed with 50 ml of diethyl ether and the ether solution was added to the separatory funnel. The water layer was separated and the ether layer was then extracted with three 25 ml portions of saturated sodium bicarbonate solution. The ether layer was separated and dried over anhydrous magnesium sulfate. The product was isolated by distillation.

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