The Reaction of Triethylaluminum with Esters

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(Received April 17, 1967)

It is the aim of the present paper to study the difference in the reactivity appearing to be present between triethylaluminum and the Grignard reagent, through experiments with esters known to have a carbonyl group of a lower reactivity than that of aldehyde or ketone, and to study if the steric effect which has been recognized in the cases of the Grignard reactions could be observed.

Experimental

All reactions were carried out in an atmosphere of dry nitrogen. The melting points were measured on a micro hot stage and were not corrected.

Materials. Commercial methyl benzoate (bp 198—199°C) and methyl phenylacetate (bp 84—85°C/6 mmHg) were purified by distillation. Ethyl 2,4,6-triethylbenzoate (bp 143—144°C/7 mmHg) was synthesized from 1,3,5-triethylbenzene *via* 2,4,6-triethylbromobenzene, 2,4,6-triethylbenzoic acid, and acid chloride.[1] *p*-Tolyl 2,4,6-triethylbenzoate (bp 205—207°C/5 mmHg) was prepared from the corresponding acid chloride and *p*-cresol. Triethylaluminum purchased from the Ethyl Corp. was used without further purification.

Reaction of Methyl Benzoate with Triethylaluminum. Methyl benzoate (0.18 mol) was added, drop by drop, to a gently refluxing 25.0 wt% solution of triethylaluminum in dry petroleum ether ($AlEt_3$ 0.37 mol). After 3 hrs' refluxing, the reaction mixture was cooled in an ice-bath, and the aluminum compound was decomposed with a theoretical amount of ethyl alcohol; then the reaction mixture was poured into an ice-cooled diluted sodium hydroxide solution. The distillation of the crude product gave 25.3 g of an oily product with a boiling point of 95—98°C/16 mmHg. The separation of alcohols in the above fraction by the method described in a previous paper[2] gave 8.1 g (33.3%) of phenylethyl carbinol and 2.2 g (12.5%) of phenyldiethylcarbinol. 3,5-Dinitrobenzoate of phenylethylcarbinol, mp 67—68°C, from ethanol, undepressed by admixture with an authentic sample. The tertiary alcohol fraction was distilled with anhydrous oxalic acid, and the dehydration product was then oxidized with an aqueous alkaline permanganate solution. 2,4-Dinitrophenylhydrazone of the oxidation product, mp 191—192°C, from diluted ethanol, was identified as that of propiophenone by a mixed melting point determination with an authentic sample.

Reaction of Methyl Phenylacetate with Triethylaluminum. The reaction of this ester with two moles of triethylaluminum yielded benzylcarbinol (phenylurethane, mp 79—80°C, from ethanol) and benzyldiethylcarbinol (phenylurethane, mp 99.5—100°C from ethanol).

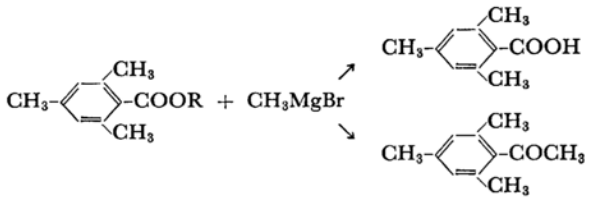
Reaction of Ethyl and the *p*-Tolyl Ester of 2,4,6-Triethylbenzoic Acid with Triethylaluminum. Ethyl 2, 4, 6-triethylbenzoate (0.05 mol) was mixed with triethylaluminum (0.114 mol) benzene solution and then the reaction solution was refluxed for 6 hr. The crude product was distilled under reduced pressure, and a fraction boiling at 127—129°C/4 mmHg (10 g) was collected. A solution of the above fraction (4 g) in 20 m*l* of glacial acetic acid was mixed with 2 m*l* of 60% sulfuric acid and the mixture was refluxed for 2 hr with stirring. The alkaline permanganate oxidation of the dehydration product gave 3.2 g of an acid substance, mp 113—114°C, from diluted ethanol, which was identified as 2, 4, 6-triethylbenzoic acid by a mixed melting point determination with an authentic sample. A reaction with the *p*-tolyl ester afforded the same product as that obtained in the above reaction.

Results and Discussion

Like Grignard reagents, triethylaluminum reacted with simple esters to give a corresponding secondary alcohol as a principal product, accompanied by tertiary alcohol. Methyl benzoate and methyl phenylacetate, for example, reacted with triethylaluminum to yield the corresponding secondary alcohol as a major product by the normal addition, followed by reduction, and a small amount of tertiary alcohol as a normal addition product.

It has been reported that, in a reaction with an aromatic ester carrying alkyl groups at both the ortho positions of the ester group, such as the mesitoic acid ester, the normal addition of a Grignard reagent to the carbonyl group of the ester function is completely inhibited and carboxylic acid or ketone is obtained as a reaction product instead of the normal product, tertiary alcohol. Fuson[3] has reported that a mesitoic acid ester (I) carrying an alkyl group as the alcohol component of the ester, for example, ethyl mesitoate, does not cause the normal addition reaction with the Grignard reagent, and the corresponding carboxylic acid is obtained as the sole reaction product. On the other hand, in the case of a mesitoic acid ester having an aryl group as the group, R, indicated in Eq. (1), for example, *p*-tolyl mesitoate, the alkyl Grignard reagent can

1) R. C. Fuson and J. Corse, *J. Am. Chem. Soc.*, **60**, 2065 (1938).
2) Y. Baba, This Bulletin, **41**, 928 (1968).
3) R. C. Fuson, E. M. Bottorff and C. B. Speck, *J. Am. Chem. Soc.*, **64**, 1450 (1942).

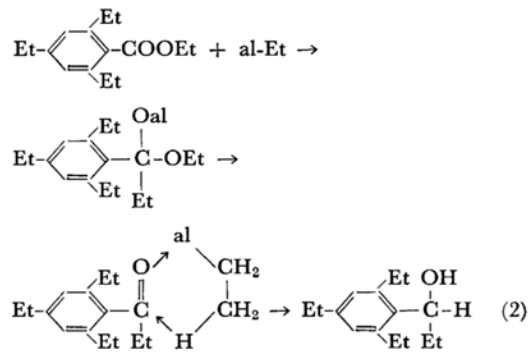


(1)

add to the carbonyl group of the ester, but the reaction product is a ketone consisting of the alkyl group of the Grignard reagent, instead of the corresponding tertiary alcohol expected from the normal addition reaction.

In the present study, it was found that ethyl 2,4,6-triethylbenzoate reacted with two molecular amounts of triethylaluminum to give neither carboxylic acid nor ketone, but a mixture of tertiary and secondary alcohols as the main reaction product. The analysis of the active hydrogen and secondary alcohol contents indicated that the secondary alcohol was the major product. That the reaction product mainly consisted of secondary alcohol was verified by the following facts. The oily product obtained from the reaction of ethyl 2,4,6-triethylbenzoate with triethylaluminum was subject to ready dehydration with 60% sulfuric acid, and the dehydration product gave the corresponding carboxylic acid, 2,4,6-triethylbenzoic acid, in a good yield by alkaline permanganate oxidation. This fact suggests that the reaction product might consist mainly of secondary alcohol or 2,4,6-triethylphenylethylcarbinol, as indicated in Eq. (2); thus, the reaction seems to proceed through the normal addition of one al-Et group to the carbonyl group of the ester followed by the reduction instead of the second normal addition of the second al-Et group.

The reaction of *p*-tolylester of 2,4,6-trisubstituted benzoic acid with triethylaluminum also differed from the corresponding Grignard reaction, the



(2)

former reaction found a parallel in the reaction with the ethyl ester of 2,4,6-triethylbenzoic acid.

It may be concluded from the results of these experiments that, in the case of a simple ester, there is practically no difference between the reaction with trialkylaluminum and that with the Grignard reagent. In the case of a sterically hindered ester, however, the reaction with triethylaluminum proceeds through the normal addition or reduction reaction as observed in the reaction of a simple ester; none of the abnormal reactions expected from the analogy of the Grignard reaction take place.

The author wishes to thank Dr. J. Yoshimura, Professor of Tokyo Institute of Technology, for his many helpful discussions and suggestions during this work.