NOTES

The Reaction of Triethylaluminum with Phthalic Anhydride

Yoshio BABA

Resources Research Institute, Kawaguchi, Saitama

(Received April 17, 1967)

In the Grignard reaction two different mechanisms have been proposed for the reaction with phthalic anhydride and for the reaction with ortho-disubstituted phthalic anhydride.

The present investigation of the reactions of triethylaluminum with phthalic anhydride, 4-methylphthalic anhydride, and 4,7-dimethylphthalic anhydride was undertaken in order to study the steric effect which has been observed in the case of Grignard reactions.

Experimental

All the 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. Triethylaluminum purchased from the Ethyl Corp. was used without further purification. Commercial phthalic anhydride (mp 131—132°C) was purified by sublimation. 4-Methylphthalic anhydride (mp 115—116°C) was synthesized from piperylene-maleic anhydride adduct *via* 4-methyl-3,4,7,8-tetrahydrophthalic anhydride and the corresponding tetrabromide.[1] 4,7-Dimethylphthalic anhydride (mp 142—143°C) was prepared by the dehydration of the 3,5-dimethylfuran-maleic anhydride adduct.[1]

Reaction of Phthalic Anhydride with Triethylaluminum. A solution of triethylaluminum (11.1 g) in dry petroleum ether (bp 35—45°C) was added, drop by drop, at room temperature into a suspension of phthalic anhydride (14.8 g) in 100 m*l* of dry petroleum ether. The solid anhydride dissolved readily, resulting in a faintly brown-colored solution. After refluxing for 1.5 hr, the reaction mixture was cooled in an ice-bath, after which the aluminum compound was decomposed by adding 17.5 m*l* of ethanol. A solid precipitate, separated on the addition of 20 g of cracked ice, was collected by suction filtration. The filter cake was washed thoroughly with ether and poured into ice-cooled, diluted hydrochloric acid. The insoluble acid substance was extracted with ether. The unchanged phthalic acid which separated out when the crude oily product (13.4 g) was left standing, was collected by filtration; mp 189—191°C, 3.8 g (22.9%). The mother liquor was distilled under reduced pressure, and a fraction boiling at 150—160°C/5 mmHg (6.2 g) was collected; it solidified on standing, mp 72—73°C, from water; it showed no depression in melting point in a mixed melting point test with phthalide.

Reaction of 4,7-Dimethylphthalic Anhydride with Triethylaluminum. The reaction of 4,7-dimethylphthalic anhydride (6.2 g) with an equimolar amount of triethylaluminum under the conditions described above gave 5.4 g of a reaction product (mp

1) M. S. Newmann and C. D. McCleary, *J. Am. Chem. Soc.*, **63**, 1543 (1941).

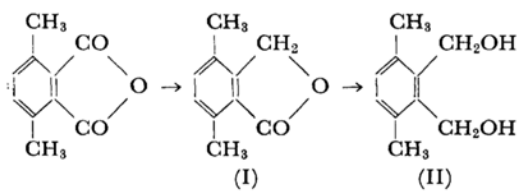
67—69°C); practically no unchanged anhydride was obtained. The recrystallization of the crude crystal from diethyl ether-petroleum ether afforded prisms, mp 72—73°C. 3,6-Dimethyl-2-α-hydroxypropylbenzoic acid.

Found: C, 69.48; H, 7.97%. Calcd for $C_{12}H_{16}O_3$: C, 69.21; H, 7.75%.

Results and Discussion

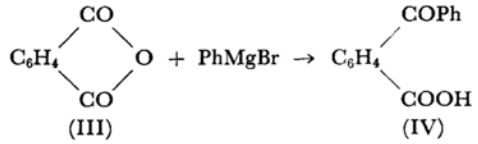
In their study of the reactions of Grignard reagents with substituted phthalic anhydride, Newman and Lord[2] have reported that, although the steric hindrance of the ortho-substituted methyl group of 4-methylphthalic anhydride was observed in the reaction with phenylmagnesium bromide, 4,7-dimethylphthalic anhydride reacted smoothly with phenylmagnesium bromide to give the expected keto carboxylic acid in a 81% yield. From the results of this experiment they concluded that, in the reaction of 4,7-dimethylphthalic anhydride, the initial addition of the Grignard reagent to the carbonyl group of the anhydride is not realized because of the steric hindrance of both methyl groups on the 4,7-positions; the reaction appears to be initiated by the cleavage of the anhydride ring.

The reduction of 4,7-dimethylphthalic anhydride with lithium aluminum hydride, however, is reported to consist of the direct reduction of the carbonyl group of the anhydride, without the initial cleavage of the anhydride ring. Buchta and Loew[3] have reported that, because of the difficulty in addition of the hydrogen to carbonyl group caused by the steric hindrance of methyl groups on the 4,7-positions, the reduction of this anhydride with lithium aluminum hydride does not proceed to the formation of the corresponding diol (II) by one step and 4,7-dimethylphthalide (I) is produced in a 88% yield.



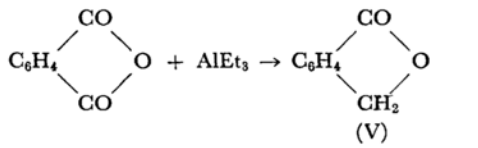
(I) (II) (1)

Phthalic anhydride (III) is known to react with one mole of phenylmagnesium bromide to give keto carboxylic acid (IV)[4]:



(III) (IV) (2)

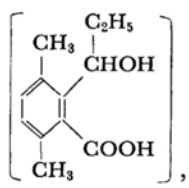
The reaction of III with an equimolar amount of triethylaluminum was found to give none of the keto acids expected from the analogy of the corresponding Grignard reaction, but afforded the reduction product or phthalide (V) in a 46.2% yield.



(V) (3)

4-Methylphthalic anhydride reacted with triethylaluminum under the same conditions as in the reaction with III to give unchanged anhydride in a 41% yield. From this apparent depression in the reactivity of 4-methyl homologue as compared with III, it might be concluded that the reaction of III and 4-methylphthalic anhydride proceeded through the direct addition of β-hydrogen of triethylaluminum to the carbonyl group.

The reaction of 4,7-dimethylphthalic anhydride with triethylaluminum found a parallel in the corresponding Grignard reaction rather than in the lithium aluminum hydride reduction. Unlike the reaction of III and 4-methyl homologue, 4,7-dimethylphthalic anhydride reacted readily with triethylaluminum under the same conditions as in the reactions with III and 4-methyl homologue, giving the product,



resulting from the addition of the ethyl group in a good yield; practically no unchanged anhydride was obtained.

2) M. S. Newmann and B. T. Lord, *J. Am. Chem. Soc.*, **66**, 733 (1944).
3) E. Buchta and G. Loew, *Ann.*, **597**, 123 (1955).
4) Bauer, *Ber.*, **38**, 240 (1905).