[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF FORDHAM UNIVERSITY]

THE ACTION OF PYRIDINE AS A CATALYST IN PERKIN'S SYNTHESIS OF CINNAMIC ACID

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Our search for a catalyst to enhance the velocity of the reaction in Perkin's synthesis of cinnamic acid led us to study the action of pyridine on the usual mixture of benzaldehyde, sodium acetate and acetic anhydride.

Twenty grams of freshly distilled benzaldehyde was mixed with 30 g. of redistilled acetic anhydride and 10 g. of anhydrous sodium acetate. To this, 8 drops of pyridine was added. The mixture was heated in a first experiment for four hours on an air-bath, a reflux condenser being used. After this, water was added (1200 cc.) and an excess of benzaldehyde distilled off by steam; 5 cc. of benzaldehyde was recovered. Concentrated hydrochloric acid was now added until the mass became acid to Congo Red. We were able then to observe a rapid precipitation of the cinnamic acid, which was filtered off by suction and dried. The yield was 18.8 g. or 67.1% of the theoretical. The acid needs no further purification, its melting point being 132°.

In a second experiment, conducted in the same way as before and using the same proportions, we continued the period of digestion for six hours and obtained 23.2 g. of cinnamic acid or 83% of the theoretical. The melting point was again 132°.

In a third experiment, the digestion was continued for a period of eight hours, everything else being equal. The result was a yield of 23.8 g. or 85% of the theoretical; melting point, 132.5°.

In each of these two latter experiments we naturally recovered a correspondingly lower amount of unchanged benzaldehyde. We have also performed experiments with a period of digestion of ten hours, but the yields were the same as in the eight-hour experiment. We can, therefore, consider the yield of the eight-hour experiment as the highest obtainable in this reaction. Furthermore, we have also conducted experiments with amounts of pyridine as large as 2 cc. but the results were the same as above.

It should be noted that the cinnamic acid thus obtained is pure and needs no further recrystallization with charcoal with its inevitable loss of material.

The following table shows a comparison of yields obtained with pyridine as a catalyst and those obtained without pyridine.[1]

The yields reported in the literature are usually given as between 15 and 20 g. with the proportions used in the above experiments, that is,

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[1] These latter experiments were performed with the collaboration of Mr. P. Conroy.

Table I

Comparison of Yields

Hours of digestion	Without pyridine Actual yield, g.	Without pyridine % of the theoretical	With pyridine Actual yield, g.	With pyridine % of the theoretical
4	10.3	36.7	18.8	67.1
6	15.00	53.6	23.2	83
8	17.00	60.7	23.8	85

between 53.6 and 70% of the theoretical; furthermore, after a digestion period of eight hours, the yield is similar to the one obtained in four hours when pyridine is used. When the digestion is continued for eight hours in the experiment with pyridine, the yield becomes 85% of the theoretical and considering also that no charcoaling is necessary, we may say that we have here a decided improvement.

Summary

A substantially increased yield (up to 85%) of cinnamic acid in the Perkin synthesis has been produced by using pyridine as a catalyst at the rate of 8 drops for 20 g. of benzaldehyde, the time of reaction being eight hours. Additional pyridine and longer heating do not increase the yield. The product is obtained in very pure condition.

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SOME SIDE REACTIONS IN THE PREPARATION OF ALKYLMAGNESIUM HALIDES

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Introduction

In connection with studies concerned with the analysis of gases evolved in Grignard reactions it is necessary to know the nature and extent of gas evolution *during the preparation* of several typical organomagnesium halides. The present paper discusses some results obtained in the preparation of methyl-, ethyl- and *n*-butylmagnesium halides.

It has long been known that in addition to the formation of RMgX compound in the reaction between RX compound and magnesium in ether, the following side reaction occurs

$$2RX + Mg \longrightarrow R{\cdot}R + MgX_2 \qquad (1)$$

Until recently this side reaction was supposed to increase markedly with the weight of the R-group and its greater branching (particularly with tertiary groups), so that with a hexyl or octyl group the extent of Reaction 1 equaled or exceeded the yield of RMgX compound.[1] Even in the

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[1] Grignard, *Ann. chim. phys.*, [7] **24**, 433 (1901).