[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY AND THE RESEARCH LABORATORY OF THE UNIVERSAL OIL PRODUCTS COMPANY]

Preparation of Dibenzyl Ketone and Phenylacetone

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Recently there was described[1] the preparation of dibenzyl ketone by heating a mixture of acetic anhydride and phenylacetic acid. Additional experience with this synthesis has shown that the method as originally published is not given in sufficient detail to ensure infallible results. These details are supplied in the present paper. It has been found also that potassium acetate is a helpful ingredient in the reaction mixture. With it, the product seems to be more easily purified than otherwise.

In addition to dibenzyl ketone it has been found that phenylacetone is also a product of the reaction. These steps account for the changes which occur

$$C_6H_5CH_2COOH + (CH_3CO)_2O \longrightarrow C_6H_5CH_2COOCOCH_3 + CH_3COOH \quad (1)$$

$$C_6H_5CH_2COOCOCH_3 \longrightarrow C_6H_5CH_2COCH_3 + CO_2 \quad (2)$$

$$C_6H_5CH_2COOCOCH_3 \longrightarrow (C_6H_5CH_2CO)_2O + (CH_3CO)_2O \quad (3)$$

$$(C_6H_5CH_2CO)_2O \longrightarrow C_6H_5CH_2COCH_2C_6H_5 + CO_2 \quad (4)$$

Phenylacetone and dibenzyl ketone evidently are pyrolytic products of phenylacetic acetic anhydride and phenylacetic anhydride, respectively. That dibenzyl ketone is formed in greater yields than phenylacetone is evidence that reaction 3 has a greater reaction rate than reaction 2. Or, if reaction 3 is an equilibrium reaction the evidence would indicate that phenylacetic acetic anhydride disappears more rapidly through reactions 3 and 4 than through reaction 2. Indirectly this may indicate that reaction 4 is faster, under the conditions obtaining in the experiment, than reaction 2.

Experimental Part

Fifty grams of phenylacetic acid was weighed into a 250-cc. three-necked flask. Then 50 g. of redistilled acetic anhydride and 2.5 g. of fused, anhydrous potassium acetate were added. A thermometer was placed in the liquid and the mixture refluxed for two hours, during which time the thermometer in the liquid registered 149–150°. A good fractionating column was inserted in place of the reflux condenser and the mixture distilled. The distillation was carried out very slowly so that the distillate was mainly acetic acid. The following table gives a typical distillation.

Time, min.	Temp., °C.		Time, min.	Temp., °C.	
	Vapor	Liquid		Vapor	Liquid
0	119	150	78	118	182
45	121	154	80	115	193
57	122	160	81	114	199
70	122.5	165	83	113	204
74	120	171			

After forty-five minutes carbon dioxide was evolved slowly. The rate increased to a maximum at about seventy-five minutes, but carbon dioxide was still being evolved slowly when the distillation was stopped. A total of 4 liters of gas was collected which was pure carbon dioxide (over 99.3% CO_2). Heating the liquid above 200–205° produced resinification with a decreased yield of ketones.

The residue was placed in a 50-cc. Claisen flask. Acetic anhydride (5 cc.) was used as a rinse. The mixture was distilled at 3 mm.: 30–75°, chiefly acetic anhydride; 75–160°, a 26-g. fraction; residue, 16 g. Redistillation (755 mm.) of the 26-g. fraction gave 8 g. (16% yield) of phenylacetone, b. p. 215–220°, and 16 g. (41% yield) of dibenzyl ketone, b. p. 317–320° (m. p. 30°). The phenylacetone was identified as the phenylhydrazone,[2] m. p. 84.5–85°.

Dibenzyl ketone may be prepared in almost the theoretical yields from phenylacetic acid by passing it over a special thoria catalyst[3] at 345°. The present method, however, possesses the advantage of simplicity and convenience which might in many instances more than make up for the lower yield.

Summary

A detailed technique is given for producing dibenzyl ketone from phenylacetic acid and acetic anhydride. Phenylacetone is formed concurrently.

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[1] Hurd, Christ and Thomas, THIS JOURNAL, **55**, 2589 (1933).

[2] Beckh [*Ber.*, **31**, 3163 (1898)] lists the m. p. as 85°.

[3] Kistler, Swann and Appel, *Ind. Eng. Chem.*, **26**, 388 (1934).