(1921), give 179–180° for the anhydrous form and an analysis of a monohydrate, for which no m. p. is recorded.

[e] Klarmann and Figdor, THIS JOURNAL, **48**, 803 (1926), give 95° for air-dried and 118° for vacuum dried at 100°. They give analysis for $C_{12}H_{10}O_4$ and do not state the degree of hydration.

[f] Karrer and Rosenfeld, *Helv. Chim. Acta*, **4**, 707 (1921), give 122° for the anhydrous form and 104° for the monohydrate.

Summary

A number of the more common alkyl cyanides have been combined with phloroglucinol in the Hoesch synthesis on a semi-micro scale to give good yields of phlorophenones which may be used conveniently as solid derivatives in the identification of the nitriles.

The ketones have been studied and their properties described.

STILLWATER, OKLAHOMA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE PREPARATION AND PROPERTIES OF TERTIARY BUTYL PHENYLACETATE

BY DAVID L. YABROFF AND C. W. PORTER

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In the course of our work on the nitration of phenylacetic acid and its esters it became necessary for us to synthesize tertiary butyl phenylacetate. This compound is not easily made by direct esterification of phenylacetic acid and hitherto its preparation has not been reported. By a modification of a method used by Houben[1] in the preparation of terpineol acetate we have succeeded in preparing pure tertiary butyl phenylacetate in yields equal to 65% of the theoretical. Since our procedure can be used to obtain other esters from tertiary alcohols and acids of high molecular weight, it seems worth while to describe the method.

A halomagnesium alcoholate is prepared by decomposing ethylmagnesium bromide with tertiary butyl alcohol

$$C_2H_5MgBr + (CH_3)_3COH \longrightarrow MgBrOC(CH_3)_3 + C_2H_6$$

The alcoholate, a white solid, is kept suspended and finely divided by vigorous mechanical stirring. An ether solution of phenylacetyl chloride is added to the ether suspension of the halomagnesium alcoholate and the reaction mixture is warmed under a reflux condenser.

$$C_6H_5CH_2COCl + MgBrOC(CH_3)_3 \longrightarrow C_6H_5CH_2COOC(CH_3)_3 + MgBrCl$$

A greater yield of the ester is obtained when the mixture is refluxed for one hour than when it is refluxed for a longer time. This is probably due to a gradual conversion of the ester into phenylacetic acid. In the longer runs we actually isolated phenylacetic acid in quantities sufficient to account for the failure to obtain a one hundred per cent. yield of the ester.

[1] Houben, *Ber.*, **39**, 1763 (1906).

Experimental

Bromomagnesium tertiary butylate was prepared in solid form by adding a slight excess of tertiary butyl alcohol to ethylmagnesium bromide and warming the mixture to drive off ethane. Most of the ether was decanted from the solid alcoholate and the rest was removed by passing dry air over the surface of the residue. The alcoholate was then dried under reduced pressure over calcium chloride. It was found to retain one molecule of ether of crystallization. The equivalent weight as determined by titration with standard silver nitrate solution (K_2CrO_4 indicator) was 234–235; calcd. for $MgBrOC_4H_9{\cdot}C_2H_5OC_2H_5$, 239.

Preparation of the Ester

Through the Grignard Reaction.—The solid halomagnesium alcoholate was allowed to react with phenylacetyl chloride with one and then the other in excess in different experiments. The time of refluxing also was varied. It made no difference in yield whether the alcoholate or the phenylacetyl chloride was in excess, but the presence of unchanged phenylacetyl chloride made the separation and purification of the ester difficult. From these preliminary experiments the following final procedure was developed.

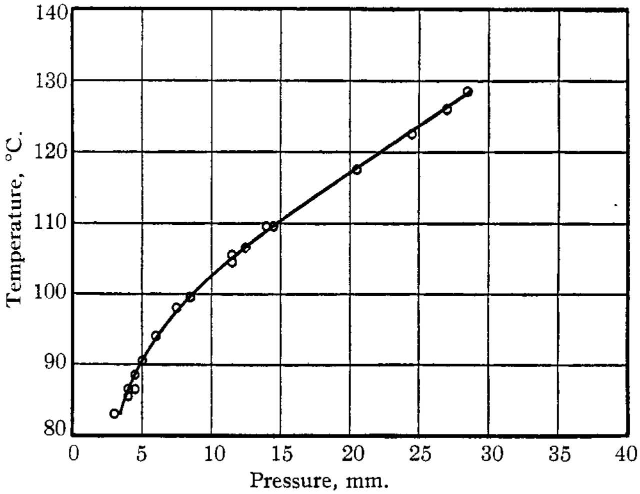

Fig. 1.—Boiling point curve for tertiary butyl phenylacetate.

A solution of 40 g. of tertiary butyl alcohol (0.54 mole) in 50 cc. of ether was added very slowly to approximately one-half mole of ethylmagnesium bromide in 300 cc. of anhydrous ether. The $MgBrOC_4H_9$ which formed as an insoluble white substance was kept in suspension by stirring. The mixture was then warmed to the boiling point of the ether and refluxed for fifteen minutes. Then 46.1 g. of phenylacetyl chloride (0.3 mole) in 50 cc. of ether was added slowly to the hot reaction mixture and refluxing was resumed for one hour.

The content of the flask was then poured on to ice and acidified with dilute sulfuric acid. The ether layer was separated, washed successively with ice-cold water, cold dilute sodium hydroxide solution, and again with cold water. A clear orange-brown liquid remained after the ether had been distilled off. This was fractionated under reduced pressure. Figure 1 shows the boiling points of the ester at various pressures.

By a Direct Method.—Phenylacetic acid was dissolved in a large excess of tertiary butyl alcohol in the presence of a small amount of concentrated sulfuric acid and the mixture was allowed to stand at room temperature for twenty days in one case and for sixty days in another case. The yields of ester obtained in this way were very small.

Refractive Index of the Ester.—Samples of approximately 25 g. of the ester from each of five preparations were separately purified by fractional distillation. Three of the preparations were made through the Grignard reaction and two were obtained by the direct esterification of the acid by the alcohol. After each fractionation the refractive index of the middle portion of each preparation was determined at 25°. Although the measurements made on different samples were not in agreement, the refractive index of each sample remained nearly constant through repeated distillations. Each preparation was then purified by dissolving the ester in ether and washing with dilute sodium hydroxide solution, dilute sulfuric acid solution, and finally with water. The ether was dried over calcium chloride, distilled off and the ester was fractionated again under reduced pressure. This treatment produced no appreciable change in the refractive index. The last trace of impurity cannot be removed from this ester by repeated washings, extractions and distillations. The refractive index may remain constant on successive distillations and still be incorrect. A similar case is seen in the values reported for tertiary butyl acetate by Henry[2] and by Smith and Olsson.[3]

Purification was finally accomplished by fractional crystallization of the compound. A sample of the ester (50 g.) was dissolved in freshly distilled pentane and the mixture was cooled with liquid air. The ester separated as a white snow-like solid. Most of the pentane (which contained about 10 g. of dissolved ester) was decanted, more pentane was added, and the process was repeated a second time. The ester obtained in the second crystallization from pentane was pure and its index of refraction was 1.4825. The density of tertiary butyl phenylacetate (d_4^{25}) was found to be 0.9758 ±0.0004, whence the molecular refraction (M_D) by the Lorentz–Lorenz equation becomes 56.19.

Melting Point of the Crystalline Ester.—When the ester is cooled with a mixture of solid carbon dioxide and ether it becomes viscous but fails to crystallize until inoculated with some of the solid ester obtained by cooling a pentane solution of the ester with liquid air. The crystals melt at -23 to $-21°$. The melting range was obtained in the usual manner by means of warming curves.

Summary

A method is described for the preparation of tertiary butyl phenylacetate which gives a yield of the purified ester equal to about 65% of the theoretical quantity. Physical properties, including boiling points at various pressures, the melting range and the refractive index of the compound have been reported. It is shown that a preparation of this ester which boils at the same temperature after repeated distillations may show a constant but erroneous refractive index.

BERKELEY, CALIFORNIA

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[2] Henry, *Rec. trav. chim.*, **26**, 438 (1907).

[3] Smith and Olsson, *Z. physik. Chem.*, **118**, 99 (1925).