

nene and dipentene, 2% cuminic aldehyde and 20% sesquiterpenes. That dipentene has been converted into caoutchouc⁶ gives some interest to the fact that these two substances occur together in *Chrysothamnus* and suggests the question, may not the one be changed into the other by the plant metabolism?

⁶ Gildemeister and Hoffman, I, p. 312.

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[CONTRIBUTION FROM THE OKLAHOMA A. AND M. COLLEGE]

IDENTIFICATION OF NITRILES. PREPARATION OF ALKYL (2,4,6-TRIHYDROXYPHENYL) KETONES BY THE HOESCH SYNTHESIS ON A SEMI-MICRO SCALE

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In a recent attempt to find an easier means of identifying alkyl cyanides, Shriner and Turner² treated them with the Grignard reagent to give liquid ketones, which were converted finally to solid semicarbazones. Although the method has been found to be satisfactory when limited amount of starting material and time are not important factors, it was thought worth while to develop here a more rapid method in which very small amounts of nitriles could be used, as is recommended by Kamm, Mulliken³ and others in qualitative organic analysis.

The present method adapts the Hoesch synthesis on a semi-micro scale, to give yields of products comparable to those described in the literature for similar preparations using much larger amounts of starting materials. Thus a small quantity of nitrile is combined with phloroglucinol to yield readily a solid phlorophenone in sufficient amount to make identification of the former very easy.

Experimental

A typical procedure for carrying out the modified Hoesch synthesis on a semi-micro scale is illustrated by the preparation of the new ketone in the series.

n-Butyl 2,4,6-Trihydroxyphenyl Ketone (Phloro-*n*-valerophenone), $C_6H_2(OH)_3-COC_4H_9$.—A solution of 0.006 mole of anhydrous phloroglucinol in about 25 cc. of dry ether was shaken up with 0.4 g. of pulverized, fused zinc chloride. To this was added 0.01 mole of *n*-butyl cyanide and a steady stream of dry hydrogen chloride gas about saturated with ether was passed through the mixture. After two to three minutes the

¹ The experimental routine of this paper was carried out largely by Mr. J. Glenn Little during an advanced course in organic preparations at Oklahoma A. and M. College.

² Shriner and Turner, *THIS JOURNAL*, **52**, 1267 (1930).

³ O. Kamm, "Qualitative Organic Analysis," J. Wiley and Sons, 1923; Mulliken, "Identification of Pure Organic Compounds," J. Wiley and Sons, N. Y., 1905.

solution turned milky and in the course of a few more minutes became clear. At the end of fifteen minutes an amber colored oil⁴ separated out. The reaction was allowed to continue for about ten minutes longer and then the supernatant liquid was decanted. The oil was taken up in 25 cc. of water and washed twice with 50 cc. of ether. The aqueous layer was concentrated to about one-half of its volume by heating. Upon cooling, long, silky needles separated which after two recrystallizations from hot water with norite gave colorless needles and when air-dried melted at 87–88° (corr.). The substance after drying in vacuum at 110° for thirty minutes or in a vacuum desiccator for a few hours lost a molecule of water to give the anhydrous ketone which melted at 149° (corr.); yield, 84.7%.

The crystals dissolved in concentrated sulfuric acid to give a deep yellow color and in dilute ferric chloride solution to form a purple-red color.

Anal. Calcd. for $C_{11}H_{14}O_4 \cdot H_2O$: H_2O , 7.9. Found: 8.2. Calcd. for $C_{11}H_{14}O_4$: C, 62.81; H, 6.72. Found: C, 62.96; H, 6.59.

The properties of the above ketone together with those of other members of the series are summarized for convenience in Table I. Each ketone gave a yellow color in concentrated sulfuric acid.

TABLE I

PROPERTIES OF KETONES OBTAINED BY THE ACTION OF 0.006 MOLE OF PHLOROGLUCINOL ON 0.01 MOLE OF NITRILE BY THE METHOD DESCRIBED

Only those nitriles studied by Shriner and Turner¹ are included here

| Nitrile | Ketone | Yield, % | M. p., °C., corr. air-dried | M. p., °C., corr. vac.-dried | Crystal form | Color in $FeCl_3$ soln. |
|--------------------------|--|----------|-----------------------------------|------------------------------------|------------------------------|-------------------------|
| CH_3CN | $C_4H_7(OH)_3COCH_3$ | 93 | 218–218.5 ^a | 218.5 ^a | Colorless needles | Cherry-red |
| C_2H_5CN | $C_6H_7(OH)_3COC_2H_5$ | 73.3 | 174–175.5 ^b | 175–176 ^b | Colorless needles | Brownish-red |
| <i>n</i> - C_3H_7CN | $C_8H_7(OH)_3COC_3H_7$ - <i>n</i> ^c | 71.7 | 180–181 ^d | 181 ^d | Colorless needles | Cherry-red |
| <i>n</i> - C_4H_9CN | $C_8H_7(OH)_3COC_4H_9$ - <i>n</i> | 84.7 | 87–88 | 149 | Colorless needles | Purple-red |
| <i>n</i> - $C_4H_{11}CN$ | $C_8H_7(OH)_3COC_4H_{11}$ - <i>n</i> | 68.5 | 95–96 ^e | 120–121 ^e | Colorless needles and plates | Purple-red |
| <i>i</i> - $C_4H_{11}CN$ | $C_8H_7(OH)_3COC_4H_{11}$ - <i>i</i> | 37.2 | 103–104 ^f | 122.5 ^f | Colorless needles and plates | Brown-red |

^a Bülow and Wagner, *Ber.*, **34**, 1798 (1901), report no melting up to 280° and give an analysis for $C_8H_8O_4$ (no hydrate); Heller, *Ber.*, **45**, 418 (1912) gives 209–210° and analysis for $C_8H_8O_4 \cdot H_2O$; Leuchs and Sperling, *ibid.*, **43**, 135 (1915), give sintering at 200° and melting at 218°, with analysis for $C_8H_8O_4$ and a monohydrate; Hoesch, *ibid.*, **48**, 1122 (1915), gives 218° and analysis for $C_8H_8O_4$ and a monohydrate; Sen and Ghosh, *J. Chem. Soc.*, **117**, 61 (1920), give 284–285° and analysis for $C_8H_8O_4$. Rosenmund and Schulz, *Arch. Pharm.*, **265**, 308 (1927), give 218° with sintering at 205°. Shriner and Kleiderer, *THIS JOURNAL*, **51**, 1267 (1929), give 213–214° (corr.) and analysis for $C_8H_8O_4$ making no mention of a hydrate although water was used as a recrystallizing solvent.

^b Canter, Curd and Robertson, *J. Chem. Soc.*, 1245 (1931), report a monohydrate and m. p. 174–175°.

^c Fabriken Vorm. Meister, Lucius and Bruning, British Patent 157,854 (1921), obtained the ketone from *n*-propyl cyanide, phloroglucinol, dry hydrogen chloride and ether, after hydrolyzing the ketimide hydrochloride by acidifying and boiling in water.

^d Karrer, *Helv. Chim. Acta*, **2**, 466 (1919), and Karrer and Rosenfeld, *ibid.*, **4**, 707

⁴ The oil, which must be a ketimide hydrochloride addition product, appeared in some of these syntheses as colorless crystals and in the preparation of phloro-*n*-caprophenone it did not appear. In the latter instance ice-cold water was added directly to the ether solution and the aqueous layer was worked up in the usual manner.

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

* 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.

[†] 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.

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

THE PREPARATION AND PROPERTIES OF TERTIARY BUTYL PHENYLACETATE

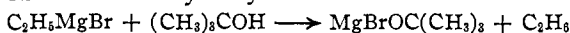
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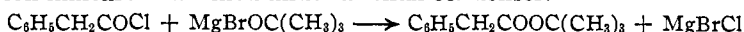
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In the course of our work on the nitration of phenylacetic acid and its esters it became necessary for us to synthesize tertiary butyl phenylacetate. This compound is not easily made by direct esterification of phenylacetic acid and hitherto its preparation has not been reported. By a modification of a method used by Houben¹ 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



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.



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).