tion of all the data, the free energy given above is probably accurate to 300 cal. and the entropy to one unit.

CAMBRIDGE, MASSACHUSETTS RECEIVED JANUARY 8, 1946

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p-Cyanostyrene

BY C. G. OVERBERGER AND R. E. ALLEN[1]

In a recent communication[2] a method of dehydrating *p*-cyanophenylmethylcarbinol to *p*-cyanostyrene was described. It has now been found that a much better yield can be obtained by first converting the carbinol to the acetate and then cracking the acetate by dropping it onto hot glass beads. The new method works best on quantities of less than 100 g.; with larger quantities polymerization during the deacetylation becomes serious.

Acetate of *p*-Cyanophenylmethylcarbinol.—Into a 200-cc. round-bottomed flask equipped with a condenser was placed 50 g. (0.34 mole) of *p*-cyanophenylmethylcarbinol and 70 g. (0.687 mole) of acetic anhydride. The mixture was treated for four hours under very gentle reflux and the contents of the flask were transferred to a 200-cc. distilling flask. The excess acetic anhydride and acetic acid were removed by distillation under water-pump pressures. The residue was then distilled through a helices-packed column. The product boiled at 154° (6 mm.); n^{20}_{D} 1.5156, d^{4}_{20} 1.0972. The yield was 58 g. (0.307 mole) or 90.3% of the theoretical amount.

Anal.[3] Calcd. for $C_{11}H_{11}O_2N$: C, 69.82; H, 5.86. Found: C, 70.08; H, 5.82.

***p*-Cyanostyrene.**—Through a vertical fifteen inch, 20-mm. Pyrex tube, packed with solid glass beads heated to 575–600° by means of an electric furnace, was dropped 58 g. (0.307 mole) of the acetate of *p*-cyanophenylmethylcarbinol to which had been added a gram of *p*-*t*-butylcatechol, at the rate of one drop per second. The distillate was collected in an ice-cooled receiver, washed twice with 100 cc. of water and twice with 100-cc. of a 10% solution of sodium bicarbonate and dried over anhydrous sodium sulfate to which was added a small amount of *p*-*t*-butylcatechol. The product was distilled through a six-inch column packed with short pieces of glass rod. The yield was 30 g. (75.8%) b. p. 92–93° (3 mm.); n^{20}_{D} 1.5772.

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[1] The work described in this note was done under the sponsorship of the Office of Rubber Reserve, Reconstruction Finance Corporation, in connection with the Government Synthetic Rubber Program.

[2] Marvel and Overberger, THIS JOURNAL, **67**, 2250 (1945).

[3] Microanalyses by Mr. H. S. Clark, Illinois State Geological Survey.

NOYES CHEMICAL LABORATORY
UNIVERSITY OF ILLINOIS
URBANA, ILLINOIS

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The Hindered Phenols

BY GORDON H. STILLSON

In an article entitled "The Hindered Phenols," by Stillson, Sawyer and Hunt,[1] an unfortunate misstatement was made. On page 304, at the conclusion of the paragraph which begins on page 303, it was stated that 2,6-di-*t*-butyl-4-methylphenol " . . . is insoluble in aqueous or alcoholic alkali of any strength." The statement intended was " . . . is insoluble in Claisen solution or in aqueous alkali of any strength." However, upon examining the latter statement critically, it occurred to us that the term "Claisen solution" does not accurately define this solvent. Claisen's directions call for dissolving 350 g. of potassium hydroxide in 250 g. of water, and making this up to 1 liter with methanol.[2] Frequently[3] Claisen used a solution consisting of 350 g. of potassium hydroxide dissolved in 400 g. of water, made up to 1 liter with methanol. Niederl[4] defines Claisen solution as "a mixture of equal parts of methanol and 50% aqueous potassium hydroxide solution." Neither author specifies the purity of the methanol used.

Now it has been found that the solubility of the hindered phenols in Claisen solution is strongly influenced by the proportion of water in the methanol which is added to the aqueous potassium hydroxide solution. Recent experiments have shown that 2,6-di-*t*-butyl-4-methylphenol is soluble to the extent of 6 g. per liter in fresh Claisen solution made up with absolute methanol. When 90 parts absolute methanol to 10 parts of water by weight is employed, the solubility drops off to only 2.7 g. per liter. 2,4,6-Tri-*t*-butyl-phenol is soluble in the amount of 2.3 g. per liter in absolute Claisen solution and 1.7 g. per liter in Claisen solution made up with 90% methanol. This solubility probably can be attributed entirely to the methanol present. The addition of water to these alcoholic alkali solutions precipitates the hindered phenols; when dilute hydrochloric acid is added to the clear filtrates from such precipitations, no further separation takes place.

On the other hand, when the isomer of 2,6-di-*t*-butyl-4-methylphenol, the so-called "cryptophenol" 2,4-di-*t*-butyl-6-methylphenol, is dissolved in Claisen solution (absolute) at its limiting concentration of 20 g. per liter, the addition of water causes negligible precipitation. The subsequent acidification with dilute hydrochloric acid brings about complete precipitation of the alkylphenol. Thus it appears that the solubility of the cryptophenol in Claisen solution comes as a result of alkali solubility rather than alcohol solubility. This Note is submitted with the approval of the co-authors.

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[1] Stillson, Sawyer and Hunt, THIS JOURNAL, **67**, 303 (1945).

[2] Claisen, *Ann.*, **418**, 96 (1919).

[3] Claisen, *ibid.*, **442**, 210 (1925).

[4] Niederl, *Ind. Eng. Chem.*, **30**, 1269 (1938).

GULF RESEARCH AND DEVELOPMENT COMPANY
PITTSBURGH 30, PA.

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Failure of the Doebner Reaction with 2-Chloro-5-aminopyridine. Synthesis of a Pyrrolidine Derivative[1]

BY MARTIN J. WEISS AND CHARLES R. HAUSER

Aniline, benzaldehyde and pyruvic acid may undergo either the Doebner cyclization, involving

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[1] The work described in this paper was done under a contract, recommended by the Committee on Medical Research, between the Office of Scientific Research and Development and Duke University.