

depress the melting point of 4-(4-chlorophenyl)-phenol, prepared by the hydrolysis of 4-(4-chlorophenyl)-phenyl acetate. The yield was 2.2 g. (67%).

The aqueous solution previously saturated with carbon dioxide was acidified with hydrochloric acid and again extracted with ether. After drying with anhydrous sodium sulfate and removing the ether, 1.4 g. of benzoic acid was obtained.

Benzoylation of 4-(4-chlorophenyl)-phenol gave rise to 4-(4-chlorophenyl)-phenyl benzoate, which did not depress the melting point of the ester prepared by the chlorination of 4-phenylphenyl benzoate.

**4-(4-Chlorophenyl)-phenyl Benzenesulfonate.**—A solution of 5 g. (10% excess) of chlorine in 100 cc. of carbon tetrachloride was introduced, drop by drop, into a solution of 20 g. of 4-phenylphenyl benzenesulfonate,<sup>4</sup> a trace of iodine, and 100 cc. of carbon tetrachloride. After the reaction mixture had been allowed to stand overnight, the solvent was removed by distillation under reduced pressure. The viscous, amber colored liquid which resulted was dried with anhydrous sodium sulfate and distilled at 8 mm. pressure. The portion which distilled between 220 and 300°, when purified with methanol, yielded 15.1 g. of crystals. After five recrystallizations from methanol, the product, m. p. 74–75°, weighed 4.7 g. (21% yield).

*Anal.* Calcd. for C<sub>13</sub>H<sub>13</sub>O<sub>3</sub>ClS: S, 9.303. Found: S, 9.309.

Reaction of benzenesulfonyl chloride with 4-(4-chlorophenyl)-phenol in pyridine yielded this same ester.

**Hydrolysis of 4-(4-Chlorophenyl)-phenyl Benzenesulfonate.**—A mixture of 3 g. of 4-(4-chlorophenyl)-phenyl benzenesulfonate and 10 g. of potassium hydroxide in 100 cc. of 50% ethanol was refluxed for ten hours, cooled and poured into 100 cc. of water. After the ethanol had been removed by distillation, the alkaline solution was extracted with ether. The ether extract was dried with anhydrous sodium sulfate and the solvent was removed by distillation under reduced pressure. No residue was left after all the ether had been removed. The aqueous solution was acidified

with hydrochloric acid and extracted with ether. After drying with anhydrous sodium sulfate and removal of the ether, 1.6 g. of light yellow solid was obtained. Three recrystallizations from chloroform and petroleum ether reduced the yield to 0.7 g. (39% yield) of a pure white solid, m. p. 145–146°. A mixed melting point with known 4-(4-chlorophenyl)-phenol caused no depression.

**Benzenesulfonylation of Certain of the Chlorinated Phenylphenols.**—A mixture of 2 g. of the phenol, 20 cc. of 10% aqueous sodium hydroxide, and 2 cc. of benzenesulfonyl chloride was refluxed for ten minutes, poured into 100 cc. of water and allowed to stand for one hour. Filtration of the product and recrystallization from ethanol yielded the ester. The results are recorded in Table I.

TABLE I  
BENZENESULFONATES FROM CERTAIN CHLORINATED  
PHENYLPHENOLS

Benzenesulfonate	M. p., °C.	Sulfur, %	
		Calcd.	Found
4-(4-Chlorophenyl)-phenyl	74–75	9.303	9.309
2-Chloro-4-phenylphenyl	59–60	9.303	9.287
2,6-Dichloro-4-phenylphenyl	128–129	8.457	8.372
2,6-Dichloro-4-(4-chlorophenyl)-phenyl	125–126	7.753	7.738

### Summary

It has been shown that chlorination of 4-phenylphenyl benzoate and 4-phenylphenyl benzenesulfonate introduces chlorine in the 4'-position of the biphenyl nucleus. Hydrolysis of the resultant chlorinated esters gave rise to 4-(4-chlorophenyl)-phenol.

The benzenesulfonates of 2-chloro-4-phenylphenol, 2,6-dichloro-4-phenylphenol and 2,6-dichloro-4-(4-chlorophenyl)-phenol were prepared for the first time.

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(4) Hazlet, *THIS JOURNAL*, **59**, 1087 (1937).

## NOTES

### The Acylation of Acetonitrile with Ethyl *n*-Butyrate and the Alcoholysis of the Resulting Ketonitrile to Ethyl *n*-Butyrylacetate

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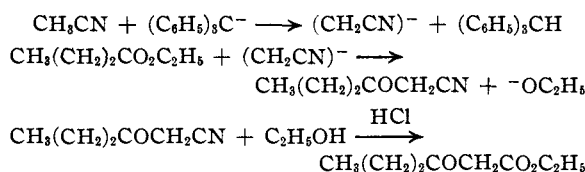
McElvain and co-workers<sup>1</sup> have shown that, in the presence of sodium ethoxide, acetonitrile (and also certain other nitriles) may be acylated satisfactorily with ethyl benzoate or ethyl iso-

butyrate to form  $\beta$ -ketonitriles, which may be alcoholized to form  $\beta$ -keto esters. Apparently, the acylation of acetonitrile with esters capable of undergoing self-condensation in the presence of sodium ethoxide, for example, ethyl *n*-butyrate, was not attempted. The acylation of the relatively reactive nitrile, phenylacetone, with ethyl acetate, however, may be effected satisfactorily.<sup>2</sup>

(1) (a) Dorsch and McElvain, *THIS JOURNAL*, **54**, 2960 (1932); (b) Cox, Kroeker and McElvain, *ibid.*, **56**, 1172 (1934).

(2) "Organic Syntheses," 1925, Vol. XVIII, p. 36.

In the present investigation it is shown that acetonitrile may be acylated with ethyl *n*-butyrate by first converting the nitrile into its anion by means of sodium triphenylmethyl<sup>3</sup> and then treating the anion with the ester; in this manner *n*-butyryl acetonitrile was obtained in 52% yield (based on the sodium triphenylmethyl). Alcoholysis of the  $\beta$ -ketonitrile gave a 64% yield of ethyl *n*-butyrylacetate, the over-all yield being 33%. The reactions may be represented as



To a stirred solution (1300 cc.) of 0.19 mole of sodium triphenylmethyl<sup>3</sup> at 0° was added 7.8 g. (0.19 mole) of acetonitrile (b. p. 81.5–82.0°) dissolved in 25 cc. of dry ether. The red color of the sodium triphenylmethyl was discharged immediately yielding a light orange solution with a white precipitate. To this stirred mixture was added during five minutes 22 g. (0.19 mole) of cold ethyl *n*-butyrate (b. p. 121.0–121.5°) dissolved in 25 cc. of dry ether. The mixture was stirred for five minutes longer, removed from the ice-bath, and shaken vigorously for two minutes. Ice water (500 cc.) was then added with shaking to the mixture, the alkaline layer separated and the ether layer washed with sodium hydroxide solution followed by water. From the dried ether solution were recovered 2.5 g. of acetonitrile and 12.0 g. of ethyl *n*-butyrate. Acidification (with cold 10% sulfuric acid) of the combined alkaline solution and washings yielded an oil. The mixture was extracted three times with ether and the combined ether solutions washed with 10% sodium bicarbonate solution, dried, and the solvent distilled. On distilling the residue *in vacuo* there was obtained 5.5 g. (52% based on the sodium triphenylmethyl) of *n*-butyryl acetonitrile boiling at 104–105° at 11 mm.

*Anal.*<sup>4</sup> Calcd. for  $\text{C}_6\text{H}_9\text{ON}$ : C, 64.8; H, 8.17. Found: C, 65.3; H, 8.21.

By allowing the reaction mixture to stand at room temperature (25°) for two days, the same yield (52%) of product was obtained, there being also formed more alkali-soluble by-product.

Treatment of the *n*-butyryl acetonitrile with dry halogen chloride in absolute alcohol<sup>1a</sup> gave a 64% yield of ethyl *n*-butyrylacetate (b. p. 94–95° at 15 mm.; copper compound, m. p. 124–125°).<sup>5</sup>

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(3) See especially Hudson and Hauser, *THIS JOURNAL*, **63**, 3156 (1941).

(4) Analysis by S. Gottlieb, Columbia University, New York, N. Y.

(5) Mqureau and Delange, *Compt. rend.*, **136**, 753 (1903); *Bull. soc. chim.*, [3] **29**, 668 (1903).

## Catalytic Hydrogenation of Cystine

BY KEVIN E. KAVANAGH

The applicability and high efficiency of the recently developed palladium and platinum synthetic high polymer catalysts were described in previous papers.<sup>1,2,3</sup> In an effort to determine whether these polymers are able to protect against the well-known poisoning of noble metals by sulfur, an attempt was made to hydrogenate cystine using a PVA-Pd catalyst. Bergmann and Michalis<sup>4</sup> reduced cystine to cysteine using palladium black: for the almost complete reduction of 4.8 g., 2 g. of palladium black and six hours of shaking were required. Applying the Pd-PVA catalyst, partial reduction of cystine was slowly obtained using only 10 mg. of Pd. Therefore, the amount of Pd was increased to 100 mg., whereupon almost complete hydrogenation resulted.

### Procedure

A catalyst containing 500 mg. of PVA, 100 mg. of Pd and 50 cc. of water was prepared. Two grams of cystine dissolved in 50 cc. of 2 *N* hydrochloric acid was introduced into the vessel and the whole shaken for forty-five hours at room temperature and ordinary pressure. At the end of this time 176 cc. of a theoretical 199 cc. of hydrogen had been absorbed. Thereupon, the still colloidal catalyst was made strongly acid with 5 cc. of 12 *N* hydrochloric acid and then flocculated by the addition of excess alcohol. The cysteine hydrochloride hydrate was isolated and air-dried. The melting point of the hydrochloride, after the molecule of water of crystallization had been removed by drying in a vacuum desiccator, was 184° decomp. The absence of cystine was ascertained by the iodometric titration of the cysteine to cystine.<sup>5,6</sup> 0.4389 g. of cysteine hydrochloric acid hydrate required 25.05 cc. of 0.1004 *N* iodine. Calcd. 24.91 I<sub>2</sub>.

*Anal.* Calcd. for the cysteine hydrochloric acid hydrate: N, 7.97; H<sub>2</sub>O, 10.25. Found: N, 7.79; H<sub>2</sub>O, 10.49.

The repeatedly emphasized<sup>4,7</sup> sensitivity of Pd catalysts to sulfur-containing proteins was smoothly overcome by using a Pd-PVA catalyst.

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(1) H. S. Taylor and W. J. Shenk, *THIS JOURNAL*, **63**, 2756 (1941).  
(2) Louis D. Rampino and F. F. Nord, *ibid.*, **63**, 3268 (1941); and forthcoming article.

(3) T. H. James, *ibid.*, **64**, 732 (1942).

(4) M. Bergmann and G. Michalis, *Ber.*, **63**, 987 (1930).

(5) Th. F. Lavine, *J. Biol. Chem.*, **109**, 141 (1935).

(6) G. Toennies and M. A. Bennett, *ibid.*, **112**, 497 (1935–1936).

(7) H. Wieland, *Ber.*, **45**, 2617 (1912); E. B. Maxted and H. C. Evans, *J. Chem. Soc.*, 603 (1937).