

manner gave 4.6 g. of 2-methyl-3,5-dimethoxybenzoic acid, m. p. 157–158° (needles from ethanol). Hetherington, *et al.*,<sup>2</sup> reported a melting point of 142–146° for V.

*Anal.* Calcd. for  $C_{10}H_{14}O_4$ : C, 61.21; H, 6.16; neut. eq., 196. Found: C, 61.35; H, 6.55; neut. eq., 195.

**2-Methyl-3,5-dimethoxybenzamide.**—A mixture of 3.8 g. of 2-methyl-3,5-dimethoxybenzoic acid and 4.0 g. of phosphorus pentachloride was allowed to stand for one hour in a loosely stoppered flask. The resulting oil was heated to 100° for one-half hour, dissolved in benzene and stirred into a mixture of cracked ice and concentrated ammonium hydroxide. The precipitate that separated was collected and recrystallized from benzene to give white needles (3.3 g.), m. p. 160–161°. Further recrystallization did not alter the melting point.

*Anal.* Calcd. for  $C_{10}H_{13}O_3N$ : C, 61.52; H, 6.71. Found: C, 61.73; H, 7.04.

**2-Methyl-3,5-dimethoxyacetophenone.**—To a Grignard reagent prepared from 1.86 g. of magnesium and 11 g. of methyl iodide in 50 ml. of dry ether was added 3.0 g. of 2-methyl-3,5-dimethoxybenzamide. The mixture was stirred in an atmosphere of nitrogen for forty hours, cooled and poured into a mixture of ice and 20% sulfuric acid. The resulting solution was boiled for one-half hour, cooled, extracted with ether, and the ether layer was washed successively with dilute solutions of sodium bisulfite, sodium bicarbonate and hydrochloric acid. The organic layer was then dried and evaporated to an oil, which was distilled at 1 mm. The distillate crystallized and was recrystallized from ether to give white prisms (2.3 g.), m. p. 46–47°.

*Anal.* Calcd. for  $C_{11}H_{14}O_3$ : C, 68.03; H, 7.27. Found: C, 68.28; H, 7.28.

**4-Methyl-5-ethylresorcinol.**—A mixture of 500 mg. of 2-methyl-3,5-dimethoxyacetophenone, 0.4 g. of potassium hydroxide, 0.5 ml. of hydrazine hydrate and 3 ml. of triethylene glycol was heated for one hour under reflux at 140°, and the temperature was raised to 185° and held there for four hours, the apparatus being set for downward distillation. At the end of this time the distillate and the material in the distilling flask were combined, flooded with water, extracted with ether, and the ether extract was washed with water, dried and evaporated to an oil. This oil was heated at reflux with 5 ml. of 48% hydrobromic acid for four hours, and the resulting solution was cooled, diluted with water, extracted with ether, and the ether layer was washed with water, dried and evaporated to an oil. Crystallization and recrystallization of the substance from water produced 200 mg. of 4-methyl-5-ethylresorcinol, m. p. 67–69°, not depressed by admixture with III from citrinin. The bis-(*p*-nitrobenzoate) of the substance was

prepared, m. p. 204–205°, not depressed by admixture with the bis-(*p*-nitrobenzoate) of III.

**Racemization of II Obtained from Citrinin.**—Citrinin (1.0 g.) was treated with acid by the procedure of Hetherington, *et al.*,<sup>3</sup> and a total of 420 mg. of II was obtained (m. p. 128–130°) along with 100 mg. of the racemate of II (m. p. 168–170°). A solution of 100 mg. of II in 100 cc. of 6 *N* sulfuric acid was boiled under reflux for four hours, cooled, and extracted with ether. The ether solution was dried, evaporated, and the resulting oil was sublimed at 1 mm. pressure. The product was then crystallized and recrystallized from an ethyl acetate–petroleum ether mixture to give 40 mg. of the racemate of II, m. p. 167–168°. A mixed melting point with the racemate of II obtained directly from citrinin produced no depression.

**Dehydration of Methyleneethylphenylcarbinol.**—Methyleneethylphenylcarbinol was prepared according to the method of Klages,<sup>20</sup> b. p. 104–105° (18 mm.),  $n_D^{20}$  1.5150. A mixture of 25 g. of the substance and 200 cc. of 4 *N* sulfuric acid solution was refluxed for four hours, cooled, extracted with ether, and the ether layer was washed with water, dried and evaporated. The product was distilled and the 2-phenylbutene-2<sup>20</sup> was collected at 83–84° (18 mm.),  $n_D^{20}$  1.5282, weight 20.3 g.

**Acknowledgment.**—The author takes pleasure in expressing appreciation to T. A. Geissman for many suggestions, to Merck & Co., Inc., for a sample of citrinin, and to Welton Burney for the analyses reported in this paper.

### Summary

The syntheses of three degradation product of citrinin have been reported, 2-ethyl-4,6-dimethoxybenzoic acid, 2-methyl-3,5-dimethoxybenzoic acid and 4-methyl-5-ethylresorcinol, the last compound by two different methods. Comparison of 4-methyl-5-ethylresorcinol with an authentic sample of degradation product prepared from citrinin proved the compounds to be identical. The properties of II (the initial degradation product of citrinin) have been shown to be compatible only with the structure 4-methyl-5-(1-methyl-2-hydroxypropyl)-resorcinol. Three possible structures for citrinin have been considered.

(20) Klages, *Ber.*, **35**, 3507 (1902).

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RECEIVED JUNE 9, 1948

## NOTES

### $\beta$ -Tetralone

BY HOMER ADKINS, A. G. ROSSOW AND JAMES E. CARNAHAN

Recent interest<sup>1,2</sup> in  $\beta$ -tetralone may make the process, used in this Laboratory<sup>3</sup> for its preparation, of some value to others.

$\beta$ -Naphthol, 500 g., in 250 ml. of dry alcohol was hydrogenated over 50 g. of copper chromium oxide at 200° under 1500 to 2500 p.s.i. until 2 moles of hydrogen per mole of

naphthol had been taken up during about five hours.<sup>4</sup> The catalyst was separated by centrifuging and the alcohol by distillation. The residue was taken up in 600 ml. of benzene and washed with ten 200-ml. portions of a 10% sodium hydroxide solution and finally with 200 ml. of water. After distillation of the benzene and 15–20 ml. of intermediate fraction, there was obtained 409 g. (80%) of product,  $n_D^{20}$  1.5632–1.5637, distilling 140–141° (13 mm.).

Dauben, McKusick and Mueller<sup>5</sup> have shown that the product so prepared and isolated may contain a few per cent. of the isomeric 5,6,7,8-tetrahydro-2-naphthol.

(1) Stork and Foreman, *THIS JOURNAL*, **68**, 2172 (1946).

(2) Birch, *J. Chem. Soc.*, 430 (1944).

(3) A. G. Rossow, Ph.D. Thesis, University of Wisconsin, 1942.

(4) Adkins and Reid, *THIS JOURNAL*, **63**, 741 (1941).

(5) Dauben, McKusick and Mueller, *ibid.*, **70**, 4179 (1948).

Pure 1,2,3,4-tetrahydro-2-naphthol has  $n_D^{25}$  of 1.5630  $\pm$  2 and a m. p. 22.9°.<sup>5</sup>

The alcohol was oxidized by transfer of hydrogen to ethylene, over a copper-zinc-nickel-barium-chromium oxide catalyst, by a method previously described.<sup>6</sup>

Equimolecular amounts of 192 g. of 1,2,3,4-tetrahydro-2-naphthol and 36 g. of ethylene together with 12 g. of the copper-zinc-nickel-barium-chromium oxide catalyst<sup>6</sup> were placed in a 1300 ml. steel reaction vessel. The mixture was heated with rocking to 250° during one hundred minutes, the pressure rising from 400 to 675 p.s.i. The reaction mixture was kept at 250° for ninety minutes and then cooled to room temperature. The products were removed from the reaction vessel with the aid of 300 ml. of ether and the catalyst separated by centrifugation. The catalyst was extracted with 100 ml. of ether and separated again. The product and the ether washings were added to a 2-l. round-bottomed flask equipped with a mechanical stirrer and containing a solution of 506 g. (4.9 moles) of sodium bisulfite in 795 ml. of water. Precipitation of the addition compound began almost at once, and after fifteen to twenty hours another portion of 96 g. of sodium bisulfite was added. The bisulfite addition compound was filtered off, washed three times by suspension in 300-ml. portions of ether and returned to the 2-l. flask where it was treated with 500 ml. of water, 240 ml. of ether and a solution of 145 ml. of concentrated sulfuric acid in 290-ml. of water. When all of the solid material had disappeared after two and one-half hours, the ether layer was separated, and the water layer was extracted with two 200-ml. portions of ether. The combined ether layers were extracted with 150 ml. of water, ten to fifteen 200-ml. portions of saturated sodium bicarbonate solution, and finally with 200 ml. of water. All but the last four or five portions of bicarbonate solution caused the ether solution to effervesce. The ether layer was dried twenty hours over 150 g. of anhydrous sodium sulfate. After the distillation of the ether, the product was distilled rapidly at 121-132° (8 mm.). The yield of  $\beta$ -tetralone,  $n_D^{25}$  1.5555, m. p. 17-18°, was 80 g. or over 40% of the theoretical. The preparation has been carried out, starting with 40 to 288 g. of 1,2,3,4-tetrahydro-2-naphthol, with yields of 35 to 42%.  $\beta$ -Tetralone was prepared by the process described, under contract OEMsr-304 with the Office of Scientific Research and Development, for the benefit of investigators of the Committee on Medical Research.

(6) Reeve and Adkins, *This Journal*, **62**, 2874 (1940).

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RECEIVED AUGUST 5, 1948

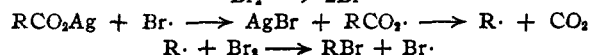
## Reactions of Silver Salts of Carboxylic Acids with Halogen

BY RICHARD T. ARNOLD AND PERRY MORGAN

Simonini<sup>1</sup> has shown that silver salts of carboxylic acids react with iodine (in a molecular ratio of 2/1) to form esters and carbon dioxide.

More recently<sup>2</sup> it has been demonstrated that these silver salts and halogens (in a molecular ratio of 1/1) afford an alkyl halide and carbon dioxide.

Price<sup>3</sup> has proposed a free radical mechanism for this transformation as follows.



(1) Simonini, *Monatsh.*, **13**, 320 (1892).

(2) Hunsdiecker and Hunsdiecker, *Ber.*, **75**, 291 (1942).

(3) Price, "Mechanisms of Reactions at Carbon-Carbon Double Bonds." Interscience Publishers, New York, N. Y., 1946, p. 55.

In the event that the  $\alpha$ -carbon atom of  $\text{RCO}_2\text{Ag}$  is asymmetric, one might expect an optically inactive alkyl bromide to result from the optically active silver salt since the tetrahedral configuration (at the  $\alpha$ -carbon atom) is lost in the formation of  $\text{R}\cdot$ .

Experimentally we have verified this fact. Both the *d*- and *l*-forms of  $\alpha$ -ethylcaproic acid when converted into their silver salts and treated with bromine (in carbon tetrachloride) yield racemic 3-bromoheptane. That no rearrangement of the carbon skeleton in the supposed  $\text{R}\cdot$  occurred was shown by converting the 3-bromoheptane into *dl*- $\alpha$ -ethylcaproic acid.

### Experimental

*d*- and *l*- $\alpha$ -Ethylcaproic Acids.—The resolution was carried out as described by Kenyon and Platt.<sup>4</sup>

*dl*-3-Bromoheptane.—The dextro form of  $\alpha$ -ethylcaproic acid (24 g.,  $[\alpha]_D^{25} +1.68^\circ$ ) was treated with dry silver acetate (29 g.) and carbon tetrachloride (475 cc.), and the suspension was refluxed for ninety minutes then cooled to room temperature. A solution of bromine (9 cc.) in carbon tetrachloride (37.5 cc.) was added slowly at first (until the induction period was terminated) and then as rapidly as possible. The whole was then heated at the boiling point for seven hours. After cooling, the solution was filtered and shaken thoroughly with aqueous sodium bisulfite containing sodium hydroxide (15 cc., 20%). Distillation gave optically inactive 3-bromoheptane; yield 10.5 g.; b. p. 50.5° (12 mm.).

Using the same procedure ( $-$ )- $\alpha$ -ethylcaproic acid (21.0 g. having a rotation of  $-3.39^\circ$  in a 2-dm. tube at 33.8°) gave optically inactive 3-bromoheptane (7.7 g.).

The above *dl*-bromides were converted to their corresponding Grignard reagents and carbonated to give *dl*- $\alpha$ -ethylcaproic acid. The amide of this compound melts at 101°.<sup>5</sup>

It is of interest to point out that *N*-(1-naphthyl)-2-ethylcaproyl amide forms beautiful crystals which melt over a range from 100-127.5° and apparently forms liquid crystal structures.

*Anal.* Calcd. for  $\text{C}_{18}\text{H}_{22}\text{ON}$ : C, 80.24; H, 8.61. Found: C, 80.13; H, 8.73.

This interesting derivative was formed from the starting *dl*- $\alpha$ -ethylcaproic acid and from each of the acid samples resulting from the inactive 3-bromoheptanes. X-Ray diffraction patterns (kindly taken by Dr. William Lipscomb of This Laboratory) were identical.

(4) Kenyon and Platt, *J. Chem. Soc.*, 633 (1939).

(5) Weizmann, Bergmann and Haskelberg, *Chem. and Ind.*, **56**, 589 (1937).

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RECEIVED JULY 26, 1948

## The Acyloin Condensation of 2-Thiophenealdehyde

BY SAMUEL Z. CARDON AND HERMAN P. LANKELMA

Grishkewitsch-Trochimowsky and I. Matschur-evitsch<sup>1</sup> applied the acyloin condensation to 2-thiophenealdehyde with negative results. It is reported that this failure to obtain thenoin is due to the instability of the thiophene ring to potassium cyanide.<sup>2</sup> In view of the stability of the thiophene ring toward other reagents there ap-

(1) Grishkewitsch-Trochimowsky and Matschur-evitsch, *J. Russ. Phys. Chem. Soc.*, **44**, 570 (1912); *C. A.*, **6**, 2406 (1912).

(2) *British Chemical Abstracts*, **102**, i, 642 (1912).