

ported for neoprotoveratrine,<sup>4</sup> yielded *p*-phenylphenacyl acetate, m.p. 110–111°, *p*-phenylphenacyl  $\alpha$ -methylbutyrate, m.p. 69–70°, and  $\alpha$ -methyl- $\alpha,\beta$ -dihydroxybutyric acid, m.p. 97–98.5°. The above compounds were further identified by mixed melting points with authentic samples and by their infrared spectra.

**Conversion of Neoprotoveratrine to Desacetylneoprotoveratrine by Methanolysis.**—Neoprotoveratrine (0.78 g.) was allowed to stand for 15 hours in methanol (100 ml.). At the end of this time, the methanol was evaporated to dryness *in vacuo* and the residue was subjected to a 24-plate countercurrent distribution using the same solvent system employed in the isolation of desacetylneoprotoveratrine. The material recovered from tubes 22–24 (0.262 g.) was crystallized from benzene, yielding clusters of needles (0.12 g.), m.p. 182–183.5°,  $[\alpha]_D^{25} -9.6 \pm 2$  (*c* 0.99 in py.). A mixed melting point with desacetylneoprotoveratrine isolated directly gave no depression. The infrared spectra of the two compounds were identical. For analysis the sample was dried at 120° (2 mm.) to constant weight.

*Anal.* Calcd. for C<sub>30</sub>H<sub>61</sub>O<sub>11</sub>N: C, 61.00; H, 8.01. Found: C, 60.99; H, 8.02.

In a volatile acid determination 16.31 mg. required 3.654 ml. of 0.01 *N* Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> or 1.72 equivalents.

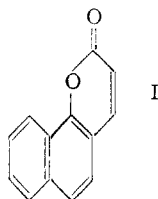
RIKER LABORATORIES, INC.  
LOS ANGELES, CALIFORNIA

### Preparation of 7,8-Benzocoumarin and 1-Methoxynaphthalene-2-propionic Acid<sup>1</sup>

By C. F. KOELSCH AND P. T. MASLEY

RECEIVED APRIL 2, 1953

$\alpha$ -Naphthol reacts with malic acid in presence of sulfuric acid to form 7,8-benzocoumarin (I)<sup>2</sup> but



the best yields so far reported<sup>3</sup> were only 25–30%. Through systematic experiments it has now been found that nearly double the previous yield can be obtained by using acetic acid as a diluent for the reaction mixture and by using an excess of malic acid.

#### Experimental

A well ground mixture of 170 g. of technical  $\alpha$ -naphthol and 226 g. of technical malic acid was added in portions during 20 minutes to a hot solution of 360 ml. of concd. sulfuric acid in 240 ml. of acetic acid. Gas evolution and some refluxing took place. During the addition and for 90 minutes afterwards, the mixture was stirred and kept at 135–141°. The solution was then stirred into one liter of crushed ice. The resulting mixture was boiled and then cooled while it was being stirred. The crude tarry product was separated, suspended in one liter of boiling water, and treated with enough sodium carbonate to cause the aqueous liquor to turn from dark brown to a reddish color. The mixture was cooled, and the solid was removed and washed with water. The product could be crystallized from acetic acid at this point, but it was usually easier to obtain a colorless product if it was distilled first, b.p. 235–240° at 6 mm., m.p. 141–142°, yield 110–127 g., 45–55%.

*Anal.* Calcd. for C<sub>18</sub>H<sub>8</sub>O<sub>2</sub>: C, 79.6; H, 4.1. Found: C, 79.9; H, 4.1.

Reduction of 35 g. of the coumarin dissolved in 200 ml. of 10% sodium hydroxide by treatment with 360 g. of 3%

sodium amalgam gave a little dimeric product and mainly 3,4-dihydro-7,8-benzocoumarin. The product was precipitated with hydrochloric acid, distilled (b.p. 210–220° at 15 mm.) and then crystallized from alcohol, yielding 29 g. of needles, m.p. 76–77°.

*Anal.* Calcd. for C<sub>18</sub>H<sub>10</sub>O<sub>2</sub>: C, 78.7; H, 5.6. Found: C, 78.7; H, 5.1.

The dihydrocoumarin reacted rapidly with phenylhydrazine in alcohol, forming 1-hydroxynaphthalene-2-propionophenylhydrazone, colorless crystals from alcohol, m.p. 176–178° dec.

*Anal.* Calcd. for C<sub>19</sub>H<sub>18</sub>N<sub>2</sub>O<sub>2</sub>: C, 74.5; H, 5.9. Found: C, 74.9, 74.2; H, 5.7, 5.9.

The dihydrocoumarin (40 g.) was methylated with aqueous sodium hydroxide and methyl sulfate, giving 80–90% of 1-methoxynaphthalene-2-propionic acid, colorless needles from ligroin containing 5% of chloroform, m.p. 94–96°, b.p. ca. 240° at 20 mm.

*Anal.* Calcd. for C<sub>18</sub>H<sub>14</sub>O<sub>3</sub>: C, 73.1; H, 6.1. Found: C, 72.8, 73.2; H, 6.1, 5.7.

1-Methoxynaphthalene-2-propionamide, colorless needles from dilute alcohol, m.p. 103–105°, was obtained from the acid with thionyl chloride and ammonium hydroxide.

*Anal.* Calcd. for C<sub>14</sub>H<sub>15</sub>NO<sub>2</sub>: C, 73.3; H, 6.0. Found: C, 73.5; H, 6.3.

SCHOOL OF CHEMISTRY  
UNIVERSITY OF MINNESOTA  
MINNEAPOLIS 14, MINNESOTA

### Direct Halogenation of Some Aromatic Amines

By GENNADY M. KOSOLOPOFF

RECEIVED MARCH 18, 1953

The complexes between dioxane and halogens which were noted by Favorskii some years ago<sup>1</sup> afford an interesting method for mild direct halogenation of sensitive aromatic compounds. We have examined the bromination of several amines by means of the dioxane–bromine complex and found that monohalogenation can be carried out with moderately good yields without resorting to the customary blocking procedure.

#### Experimental Part

The complex, an orange-yellow solid, m.p. 64°, is readily prepared in quantity by mixing equimolar amounts of the components and quenching the hot product in ice-water. However, if the material is to be used in solution, it is merely necessary to add the desired amount of bromine to a cooled and stirred mass of dioxane. The bromination of amines can be carried out either by direct addition of the finely powdered complex to a solution of the amine, preferably in dioxane, or by addition of a dioxane solution of the complex to a cooled and stirred solution of the amine in dioxane in the presence of the requisite amount of concentration aqueous alkali. The latter procedure appears to be more economical of the amine.

**Aniline.**—The complex (25 g.) was added over 15 minutes in its original crystalline state (crystals 1–2 mm. diameter) to 9.3 g. of aniline in 20 g. of dioxane at 5–10° with stirring, in a beaker. The resulting precipitate was filtered off, washed with a little water and dilute sodium hydroxide, and again with water. The product (7 g.) was then dissolved in 75 ml. of hot ethanol and cooled, yielding 1.75 g. of 2,4,6-tribromoaniline. The solution was diluted with two volumes of water and on cooling yielded 4.5 g. (26%) of *p*-bromoaniline, m.p. 66.0–66.5°, characterized by mixed melting point with an authentic specimen and further by conversion to the acetyl derivative, which melted at 165°.

When the above experiment was repeated with finely ground complex which permitted more rapid solution and better distribution of the halogenating agent in the mixture, yields up to 50–57% were obtained and the amount of tribromoaniline declined to a small fraction of a gram.

(1) From the M.S. Thesis of Paul Thomas Masley, July, 1942.

(2) V. Pechmann, *Ber.*, **17**, 1651 (1884).

(3) K. Bartsch, *ibid.*, **36**, 1966 (1903).

(1) A. E. Favorskii, *J. Russ. Phys. Chem. Soc.*, **38**, 741 (1906).