

The N-ethyl derivative was made by gently refluxing for three days a mixture of 6.7 g. of the dry silver salt, 3.7 g. of ethyl iodide and 50 cc. of absolute ether. The unchanged imide was removed by extraction with sodium bicarbonate solution. The insoluble portion was dissolved in ether, 10 cc. of alcohol was added and the product was crystallized repeatedly by evaporation of the ether; yield, 1.4 g.; m. p. 191–192°.

The N-benzyl derivative was made by refluxing overnight a solution of 5.8 g. of the sodium salt and 2.53 g. of benzyl chloride in 25 cc. of alcohol. Crystallized from alcohol it melts at 169–170°; yield, 5.6 g.

*Anal.* Calcd. for  $C_{17}H_{15}O_2NBr$ : N, 3.91. Found: N, 3.89.

A sample of the imide (1.34 g.) oxidized by a boiling mixture of 5 cc. of nitric acid (1.42) and 5 cc. of water gave 0.8 g. of *p*-bromobenzoic acid which after crystallization from alcohol melted at 254°. The same acid was obtained by refluxing a solution of the imide (0.67 g.) prepared from 0.21 g. of sodium bicarbonate and 10 cc. of water, while 200 cc. of a 1% solution of potassium permanganate was added during a period of 2.5 hours.

To an ice-cold solution of 1.2 g. of sodium hydroxide in

10 cc. of water was added 2.68 g. of *p*-bromophenylhydroxymaleic imide. As it was stirred the red solution became colorless. The mixture was allowed to stand for one day. The products were ammonia, sodium oxalate and *p*-bromophenylacetic acid; m. p. 113–114°.

Phenylhydroxymaleic imide prepared by the method of Bougault was dissolved in 75 cc. of nitrobenzene. To this solution was added 1.8 cc. of bromine. After heating a short time the mixture was allowed to stand for three days at room temperature. The crystals were separated from the mother liquor by decantation and recrystallized from alcohol; yield, 4.3 g.; m. p. 239–240°.

### Summary

The action of bromine on ethyl cyanophenylpyruvate leads to the formation of *p*-bromophenylhydroxymaleic imide. The identity of the product has been established by its hydrolysis to *p*-bromophenylacetic acid, its oxidation to *p*-bromobenzoic acid and its formation by the action of bromine on phenylhydroxymaleic imide.

NEWARK, DELAWARE

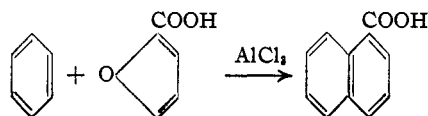
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[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

## The Reaction of Furoic Acid with Tetralin

BY CHARLES C. PRICE AND NORMAN C. DENO

Since the reaction of furoic acid and aluminum chloride with various aromatic compounds of the benzene series was found to produce naphthoic acids,<sup>1</sup> the reaction has been extended to the

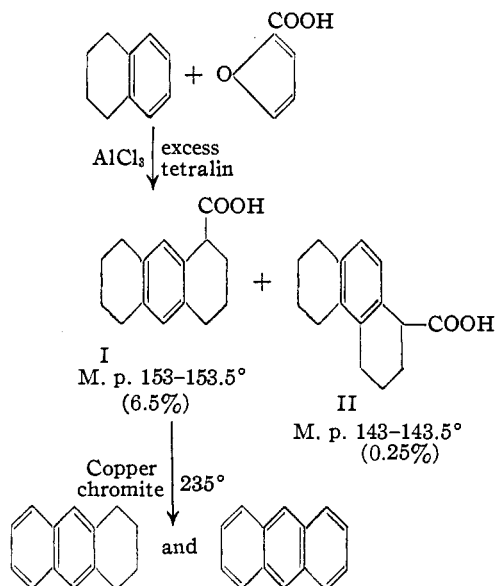


naphthalene series, in the expectation of obtaining phenanthroic or anthroic acids.

From naphthalene, furoic acid and aluminum chloride, the only product obtained was an intractable amorphous, neutral black powder, but from the condensation of tetralin and furoic acid it was possible to isolate two isomeric crystalline acids. These acids had four more hydrogen atoms than the expected tetrahydroanthroic or phenanthroic acids. Evidently, disproportionation of hydrogen occurred with the excess tetralin used as solvent for the condensation.

The crystalline product obtained in greater yield (6.5%), shiny white plates melting at 153–

153.5°, has been shown by simultaneous decarboxylation and dehydrogenation with copper chromite catalyst to contain an anthracene nucleus and thus appears to be *sym*-octahydro-1-anthroic acid (I). The most likely structure for the isomeric product, slender needles melting at



(1) Gilman, McCorkle and Calloway, *THIS JOURNAL*, **56**, 745 (1934); McCorkle and Turck, *Proc. Iowa Acad. Sci.*, **43**, 205 (1936); Price, Chapin, Goldman, Krebs and Shafer, *THIS JOURNAL*, **63**, 1857 (1941).

143–143.5°, would appear to be that of *sym*-octahydro-1-phenanthroic acid (II).

Although the crystalline acids isolated represented only about one-tenth of the total acidic product formed in the reaction, no other crystalline material could be isolated from the residue.

### Experimental<sup>2</sup>

***sym*-Octahydro-1-anthroic Acid (I).**—A suspension of 48 g. (0.43 mole) of furoic acid in 400 cc. of tetralin was stirred in an ice-bath while 120 g. (0.90 mole) of aluminum chloride was added in small portions. After the aluminum chloride had been added, the deep red-black viscous reaction mixture was stirred at 50–60° for twelve hours or at room temperature for forty hours. The reaction mixture was poured into 400 cc. of hydrochloric acid and 400 g. of ice and was stirred at 50–60° for six hours to complete hydrolysis. One liter of benzene was added and the deep red, green-fluorescent solution was extracted with sodium bicarbonate solution; 0.3 g. of *sym*-octahydro-1-anthroic acid was recovered from this extract by acidification. The benzene was then extracted with three 200-cc. portions of 2% sodium hydroxide and the red, blue-fluorescent extract was acidified; 68 g. of a pale tan tacky solid precipitated. This material, which had a neutral equivalent of 335, was redissolved in alkali and fractionally precipitated, either with hydrochloric acid or carbon dioxide. The brown gum first precipitated was removed by filtration. Further acidification gave about 10 g. of white solid which was recrystallized three times from 50% ethyl alcohol, yield, 6.2 g. (6.3%) of shiny white plates of *sym*-octahydro-1-anthroic acid (I), m. p. 153–153.5°.

*Anal.* Calcd. for C<sub>15</sub>H<sub>14</sub>O<sub>2</sub>: C, 79.62; H, 6.24; neut. eq., 226. Calcd. for C<sub>15</sub>H<sub>18</sub>O<sub>2</sub>: C, 78.23; H, 7.87; neut. eq., 230. Found: C, 78.31; H, 8.01; neut. eq., 230.

Treatment of this acid (I) by the procedure used for the dinitration of durene<sup>3</sup> gave an acid melting from 230 to 235° with a neutral equivalent of 333. The neutral equivalent for 9,10-dinitro-octahydro-1-anthroic acid should be 320.

**Decarboxylation.**—A solution of 0.5 g. of the anthroic acid (I) in 5 cc. of quinoline was heated for eighteen hours at 235° in the presence of 0.2 g. of copper chromite catalyst. The mixture was cooled, ether was added and the solution washed with several portions of dilute hydrochloric

acid and sodium hydroxide. The ether was dried, treated with Norite, which removed most of the color, and then evaporated. The tetrahydroanthracene, 0.2 g., was recrystallized from 70% alcohol as white plates, m. p. 102–104°. Because of the similarity of melting point and appearance, a mixture of the decarboxylation product and phenanthrene, m. p. 101–102°, was prepared; it melted at 84–99°. A second decarboxylation, apparently identical with that described above, gave some anthracene, identified by melting point and mixed melting point.

When one gram of the anthroic acid was heated with 0.56 g. of sulfur at 180–190° for ten hours, hydrogen sulfide was evolved copiously. The residue was dissolved in 50 cc. of benzene and the solution was filtered and extracted with sodium bicarbonate. Acidification of this extract precipitated 0.4 g. of orange-yellow powder, m. p. 216–226°. Purification of this material could not be effected by crystallization from alcohol, acetic acid or benzene. Sublimation at 205–210° yielded beautiful long, slender, clear-yellow needles,<sup>5</sup> but the melting point was the same as that of the crude product. Qualitative tests for sulfur by sodium fusion were negative.

***sym*-Octahydro-1-phenanthroic Acid (II).**—When the mother liquor from the first recrystallization of the octahydroanthroic acid (I) was allowed to evaporate slowly clusters of needles separated among the plates. After mechanical separation and six recrystallizations from 50% alcohol, the slender shiny needles obtained (0.25 g. or 0.25%) melted at 143–143.5°.

*Anal.* Calcd. for C<sub>15</sub>H<sub>18</sub>O<sub>2</sub>: C, 78.23; H, 7.87; neut. eq., 230. Found: C, 78.46; H, 7.56; neut. eq., 233.

### Summary

The reaction of furoic acid with tetralin in the presence of aluminum chloride gave a considerable amount of acidic product from which two isomeric crystalline acids were obtained in small yield. These acids contained four more hydrogen atoms than had been expected and are believed to be *sym*-octahydro-1-anthroic and 1-phenanthroic acids.

URBANA, ILLINOIS

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(4) Schroeter [*Ber.*, **57**, 2013 (1924)] has reported the melting point of tetracene (tetrahydroanthracene) as 103–105°.

(5) Graebe and Blumenfeld, *ibid.*, **30**, 1118 (1897), and Liebermann and Pleus, *ibid.*, **37**, 648 (1904), report that 1-anthroic acid sublimes as clear yellow needles melting at 245°.

(2) Microanalyses by L. G. Fauble and Theta Spoor.

(3) Smith, "Org. Syntheses," **10**, 40 (1930).