

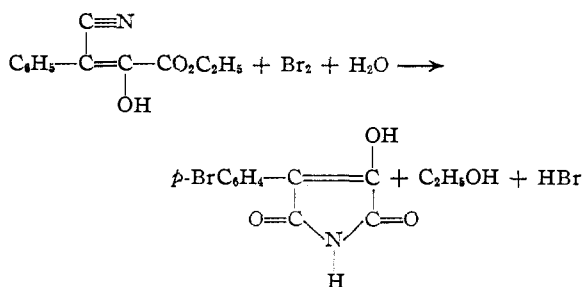
[CONTRIBUTION FROM THE CHEMICAL LABORATORY, UNIVERSITY OF DELAWARE]

*p*-Bromophenylhydroxymaleic Imide

BY GLENN S. SKINNER, C. A. COGLAN AND A. S. BERLIN

Bromine reacts with ethyl cyanophenylpyruvate in chloroform solution to give a colorless unstable addition product. The initial reaction is followed by the loss of hydrogen bromide. The products then undergo a series of reactions to yield *p*-bromophenylhydroxymaleic imide. This is a lemon-yellow crystalline substance whose brick-red sodium salt reacts with benzyl chloride in alcohol to give a benzyl derivative. The silver salt reacts with ethyl iodide in absolute ether to give an ethyl derivative. The nature of the reaction product is further attested by its oxidation to *p*-bromobenzoic acid and its alkaline hydrolysis to *p*-bromophenylacetic acid.

As to the mechanism of its formation, the first step in the breakdown of the addition product involves the loss of hydrogen bromide and the formation of the amide. The tertiary bromine atom then rearranges to the ring at this point or during cyclization. It is significant that this bromine atom appears exclusively in the para position since this is typical of the rearrangement of many similarly placed atoms or groups in the aromatic series. Ring formation takes place through the loss of alcohol. In the case of ethyl cyanomethylpyruvate<sup>1</sup> ethyl alcohol is not lost and the final product is ethyl  $\beta$ -bromo- $\beta$ -carbamido- $\alpha$ -keto-butyrate. The last two steps are similar to the formation of phenylhydroxymaleic imide from the unbrominated ester by the action of cold concentrated sulfuric acid in alcohol.<sup>2</sup> The cyclization and bromination may also proceed partly in the reverse order as the same product is obtained by bromination of phenylhydroxymaleic imide. The reaction may be formulated as follows

(1) Wislicenus and Silberstein, *Ber.*, **43**, 1834 (1910).(2) Bougault, *J. Pharm. Chem.*, **10**, 297 (1914).

## Experimental

**Bromination of Ethyl Cyanophenylpyruvate.**—A hot solution of 21.7 g. of the ester in 80 cc. of dry chloroform contained in a 250-cc. bulb connected to a condenser by a glass joint was rapidly cooled to 45–50° in a water-bath. Water (1.8 cc.) and dry bromine (5.3 cc.) were added simultaneously with good mixing in the course of a few minutes. The reaction was rapid with the evolution of hydrogen bromide and initially a colorless almost entirely liquid layer may separate at the bottom in the absence of continued agitation. The mixture was kept at approximately 50° for six hours and then allowed to stand for two days at room temperature. A slight excess of bromine remained at the end of the reaction. The chloroform was decanted and the crystalline product was crystallized from boiling alcohol. The yield of lemon-yellow crystals was 22 g.; m. p. 239–240°.

*Anal.* Calcd. for  $\text{C}_{10}\text{H}_8\text{O}_3\text{NBr}$ : N, 5.22. Found: N, 5.15.

There was no lachrymatory effect of bromobenzyl cyanide from the residues in the mother liquor when the experiment was conducted in the above manner. The yield dropped to about 9 g. when the added water was omitted. In this case the residues had a powerful lachrymatory effect. Small amounts of ammonium bromide were always formed. The product was obtained in approximately the same yield from the methyl and *n*-butyl esters. An equivalent amount of the alcohol was isolated by extraction of the chloroform with water followed by salting out with potassium carbonate. Ethyl alcohol was further identified as a reaction product of the ethyl ester by conversion to the 3,5-dinitrobenzoate; m. p. 78–79°. No *o*-bromophenylhydroxymaleic imide could be isolated from the combined mother liquors.

**Characterization of *p*-Bromophenylhydroxymaleic Imide.**—The imide is slowly soluble in cold sodium bicarbonate solution and very soluble in ether. It is stable to cold dilute permanganate and to bromine water. The sodium salt was obtained in 88% yield by the following procedure: *p*-bromophenylhydroxymaleic imide (53.6 g.) was dissolved in a hot solution of 12.4 g. of sodium carbonate in 150 cc. of water. The solution was filtered hot and allowed to crystallize. The brick-red crystals were filtered with suction and washed with a 1:2 alcohol-ether mixture. The product was recrystallized from an alcohol-water mixture. The salt decomposes at 321°. For the analysis it was dried to constant weight at 110°.

*Anal.* Calcd. for  $\text{C}_{10}\text{H}_7\text{O}_3\text{NBrNa}$ : Na, 7.93. Found: Na, 7.92.

The brick-red gelatinous silver salt was precipitated quantitatively from an aqueous solution of the sodium salt. It was dried in a vacuum desiccator protected from light under the influence of which its color changes to chocolate-brown.

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  $C_{17}H_{13}O_2NBr$ : 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

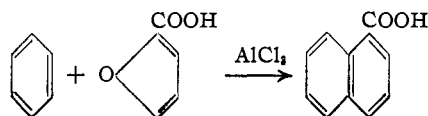
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[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

## 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

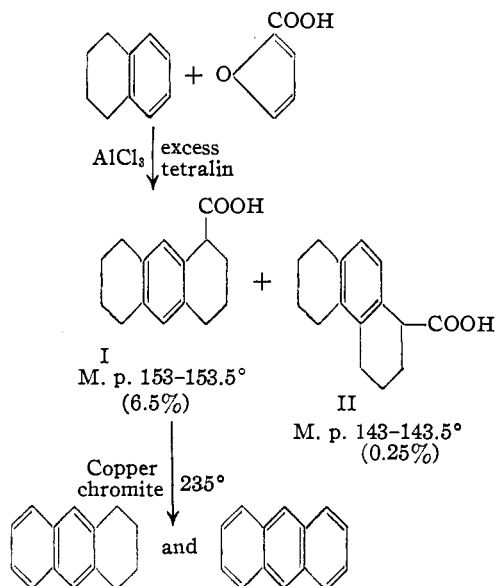


naphthalene series, in the expectation of obtaining phenanthroic or anthroic acids.

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).