

The salts obtained by the addition of two moles of *d*-bromocamphorsulfonic acid to one of chloroquine were low melting, hygroscopic, finely divided, and somewhat unstable crystals. This made handling difficult and some mechanical loss unavoidable. The quality of the *d*-bromocamphorsulfonic acid was also of great importance and the poor results of some runs was supposed due to slight decomposition during preparation of the free acid. The enantiomorphs of the drug are much more soluble than the racemic mixture.

Neither of the optically active forms submitted to the Survey Office showed any significant differences<sup>3</sup> in antimalarial activity in birds and for toxicity in dogs from the racemate.

#### Experimental

**Starting Materials.**—Chloroquine diphosphate was kindly furnished by Dr. R. C. Elderfield of Columbia University. The free base was liberated from an aqueous solution of the salt with ammonia and was recrystallized from benzene and hexane. We are indebted to Dr. H. R. Snyder of the University of Illinois for the ammonium salt of *d*-bromocamphorsulfonic acid. The free acid was liberated from the salt by the method of Pope and Peachey.<sup>4</sup>

A solution was made of 21 g. of chloroquine and 45 g. of *d*-bromocamphorsulfonic acid in 300 ml. of hot absolute ethanol. The solution was filtered to remove any insoluble material and then allowed to crystallize in a cold room. The crystals were separated rapidly by filtration and recrystallized from about 150 ml. of absolute ethanol to a constant rotation of  $[\alpha]_D^{25} + 62^\circ$  (0.200 g. was made up to 10 ml. with water). The base was obtained by dissolving the salt in water, adding an excess of ammonia, and extracting with benzene. The benzene solution was filtered and mixed with an equal volume of petroleum ether (b.p. 80–100°). The solution was concentrated until crystallization took place upon standing in the cold room. The crystals (9.7 g.) melted at 84–86°;  $[\alpha]_D^{25} + 12.3^\circ$  (0.200 g. was made up to 10 ml. with 95% ethanol).

The *l*-form of the drug was liberated by evaporating the mother-liquor from the crystalline salt almost to dryness, dissolving in water, and treating as above. The concentration of the benzene and petroleum ether solution was adjusted so as to precipitate about one gram of solid in the cold. This material, almost inactive, was discarded and the solution was concentrated further. On cooling, 4.3 g., m.p. 84–87°, of the *l*-form separated;  $[\alpha]_D^{25} - 13.2^\circ$  (0.200 g. made up to 10 ml. with 95% ethanol).

(3) F. Y. Wiselogle, "A Survey of Antimalarial Drugs," J. W. Edwards, Ann Arbor, Michigan, 1946, p. 388.

(4) W. J. Pope and S. J. Peachey, *J. Chem. Soc.*, **78**, 893 (1898).

DEPARTMENT OF CHEMISTRY  
NORTHWESTERN UNIVERSITY  
EVANSTON, ILLINOIS

RECEIVED OCTOBER 29, 1948

### An Improved Laboratory Preparation of Copper-Chromium Oxide Catalyst

BY THOMAS W. RIENER<sup>1</sup>

During the course of an investigation<sup>2</sup> of copper chromium oxides as a catalyst for hydrogenation of fatty esters to alcohols, a very satisfactory laboratory procedure for the decomposition of the copper ammonium chromate was developed. A

(1) Present address: Industrial Rayon Corporation, Cleveland, Ohio.

(2) Work done at Rohm & Haas Company.

catalyst of high activity and long life was obtained by this improved technique.

The method described here is similar to that previously reported<sup>3</sup> except that the decomposition of the copper ammonium chromate is carried out under carefully controlled conditions. If excessive temperatures are reached during the decomposition of the copper ammonium chromate, the activity of the catalyst is seriously affected.

A batch of copper ammonium chromate was prepared in the usual manner<sup>3</sup> and divided into several portions. A portion (I) was placed in a muffle furnace at 320° and in a short time the temperature inside the mixture reached 635°. Another portion (II) was fired as described below at 400°. A third portion (III) was similarly fired at 350°.

The catalysts obtained in each experiment were used in the hydrogenation of the lauryl ester of coconut oil fatty acids. The reductions were carried out in a 480-cc. Parr Instrument shaking bomb using 2 g. catalyst and 80 g. ester and run for two hours at 275°/3000 lb. H<sub>2</sub>: (I) gave 30.5% hydrogenation; (II) gave 88.3% hydrogenation; (III) gave 92.1% hydrogenation.

#### Experimental

A solution of 260 g. of copper nitrate (Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O) in 900 cc. of tap water at 80° was added while stirring to a solution of 178 g. of sodium dichromate (Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>·2H<sub>2</sub>O) and 225 cc. of 28% ammonium hydroxide made up to 900 cc. at 25°. The precipitate was collected on a Buchner funnel and washed by slurring in water three times. The copper ammonium chromate was dried at 75–80° overnight.

The copper ammonium chromate was powdered and added in small portions to a one-liter three-neck flask equipped with a stainless steel stirrer of the crescent type which scraped close to the bottom of the flask. The flask was partially immersed in a Woods metal-bath heated at 350°. The time of addition was fifteen minutes. The mixture was heated and stirred at 350° for fifteen minutes after all of the complex had been added. It was then passed through a 200-mesh screen with the aid of a camel's hair brush.

(3) Connor, Folkers and Adkins, *THIS JOURNAL*, **54**, 1138 (1932).

RESEARCH LABORATORIES

ROHM & HAAS COMPANY RECEIVED JANUARY 25, 1949  
PHILADELPHIA, PENNSYLVANIA

### The Effect of Heat and Sodium Sand upon Sodium Polybutadiene<sup>1</sup>

BY ROBERT M. ROSS

The percentage of external double bonds in sodium-polymerized polybutadiene has been shown to be dependent upon the temperature of polymerization.<sup>2,3</sup> Polybutadiene, polymerized with sodium at 30°, contains 65–75% external

(1) The work described in this manuscript was done under the sponsorship of the Office of Rubber Reserve, Reconstruction Finance Corporation, in connection with the Government Synthetic Rubber Program. The author is deeply indebted to Dr. C. S. Marvel for initiating this investigation, as well as for his advice during the course of the work.

(2) Ziegler, Grimm and Willer, *Ann.*, **542**, 90 (1939).

(3) Kolthoff, Lee and Mairs, *J. Polymer Sci.*, **3**, 220 (1947).