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 enantimorphs 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[3] 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.[4]

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 $[\alpha]^{27}\mathrm{D} + 62°$ (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°; $[\alpha]^{25}\mathrm{D} + 12.3°$ (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; $[\alpha]^{27}\mathrm{D} - 13.2°$ (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.*, **73**, 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[1]

During the course of an investigation[2] 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 catalyst of high activity and long life was obtained by this improved technique.

The method described here is similar to that previously reported[3] 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[3] 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_2: (I) gave 30.5% hydrogenation; (II) gave 88.3% hydrogenation; (III) gave 92.1% hydrogenation.

Experimental

A solution of 260 g. of copper nitrate ($Cu(NO_3)_2{\cdot}3H_2O$) in 900 cc. of tap water at 80° was added while stirring to a solution of 178 g. of sodium dichromate ($Na_2Cr_2O_7{\cdot}2H_2O$) 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 slurrying 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.

---

[1] Present address: Industrial Rayon Corporation, Cleveland, Ohio.

[2] Work done at Rohm & Haas Company.

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

RESEARCH LABORATORIES
ROHM & HAAS COMPANY
PHILADELPHIA, PENNSYLVANIA

RECEIVED JANUARY 25, 1949

The Effect of Heat and Sodium Sand upon Sodium Polybutadiene[1]

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.[2,3] Polybutadiene, polymerized with sodium at 30°, contains 65–75% external

---

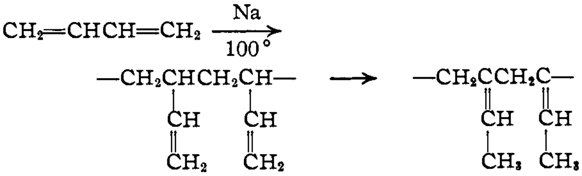
[1] The work described in this manuscript was done under the sponsorship of the Office of Rubber Reserve, Reconstruction Finance Corporation, in connection with the Government Synthetic Rubber Program. The author is deeply indebted to Dr. C. S. Marvel for initiating this investigation, as well as for 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.*, **2**, 220 (1947).

double bonds, whereas the polymer formed at 110° possesses about 15% external double bonds. In direct contrast to the product obtained from the sodium-catalyzed polymerization of butadiene, the terminal double bond percentage of polybutadiene, formed by emulsion methods, has been found to be independent of the polymerization temperature.[3]

Ziegler, Grimm and Willer[2] have explained these facts on the basis that at higher temperatures an increased amount of 1,4-addition occurs in the sodium-catalyzed polymerization. Another possible explanation is that the relative amount of 1,2- or 1,4-addition remains constant, but that an allylic rearrangement occurs in the presence of sodium so as to transform terminal methylene groups into ethylidene groups



$$CH_2{=}CHCH{=}CH_2 \xrightarrow[100^\circ]{Na} \underset{\underset{CH_2}{\|}\ \ \ \ \underset{CH_2}{\|}}{\underset{CH\ \ \ \ \ \ CH}{|\ \ \ \ \ \ \ |}}{-CH_2CHCH_2CH-} \longrightarrow \underset{\underset{CH_3}{|}\ \ \ \ \underset{CH_3}{|}}{\underset{CH\ \ \ \ CH}{\|\ \ \ \ \ \|}}{-CH_2CCH_2C-}$$

Accordingly it was the objective of this work to learn if preformed polybutadiene, prepared by sodium-catalysis methods, showed a decrease in the percentage of terminal double bonds when it was treated with sodium and heated. When sodium-polymerized polybutadiene was heated to 110° for five hours in the presence of sodium sand, analysis by perbenzoic acid titration[4] of the product obtained indicated that no appreciable double bond shifts from external-to-internal positions had occurred. Similar results were obtained when butadiene was polymerized in the presence of sodium sand at 30° and then heated to 100° for five hours.

It may be concluded, therefore, that an allylic shift, catalyzed by sodium, is not responsible for the difference in the products obtained from the sodium-catalyzed polymerization of butadiene and polybutadiene prepared by emulsion methods. Furthermore, since the terminal double bond percentage in polybutadiene formed by emulsion methods is independent of polymerization temperature, the two polymerization methods must proceed by different mechanisms.[5]

Experimental

Attempted Isomerization of Sodium Polybutadiene with Sodium Sand.—In a 500-ml., three-necked, round-bottomed flask were placed 3 g. of sodium-polymerized polybutadiene,[6] which had been reprecipitated by ethanol from benzene solution, and 250 ml. of redistilled toluene (b. p. 110–111°). The flask was equipped with a glass-sleeved Hershberg stirrer and reflux condenser. Solution was complete after about fifteen hours. At the end of this time, 0.3 g. of freshly cut sodium metal was added to the toluene solution. The contents of the flask were heated to the reflux temperature, and at this point vigorous stirring was commenced. The sodium was dispersed to a fine sand. The reaction mixture was then maintained at the reflux temperature with continuous stirring for five hours. At the end of this time, the mixture was allowed to cool to about 30°. A small amount of tarry material formed during the heating period. The excess sodium was destroyed by the addition of 100 ml. of absolute ethanol and stirring was stopped.

The insoluble macrogel and tarry material which had formed during the course of the experiment were removed by filtration through a wire screen. The filtrate was added in a fine stream to a rapidly stirred solution of 2 g. of phenyl β-naphthylamine in 1 liter of ethanol. The precipitated polymer was washed with 200 ml. of 0.2% phenyl β-naphthylamine in ethanol and finally dried at 80° for one hour under a reduced pressure of less than 1 mm. The dried polymer weighed 2.3 g. and was stored away from light and in a desiccator under reduced pressure. The polymer thus obtained and the reprecipitated polymer employed as starting material were analyzed for external double bonds by perbenzoic acid titration.[4] The results of the analyses expressed as % external double bonds are as follows: reprecipitated sodium-polymerized polybutadiene, 71.2%; reprecipitated sodium-polymerized polybutadiene, heated with sodium sand for five hours, 66.8%.

Polymerization of Butadiene and the Subsequent Application of Heat to the Sodium Polybutadiene Formed.—The sodium sand-catalyzed polymerization of butadiene was carried out according to the directions of Marvel, Bailey and Inskeep.[7] In conducting this experiment, two simultaneous and analogous polymerizations were carried out at 30° for twenty-one hours using about 0.4% by weight of sodium sand in terms of the weight of butadiene. At the end of this time, the polymerization bottles were removed from the constant temperature bath and chilled to 0°. One polymerization bottle was opened, flushed out with nitrogen, recapped, and finally heated on a water-bath for five hours at 100°. At the end of this time, the bottle and contents were cooled to room temperature and opened. The excess sodium was destroyed by the addition of 100 ml. of a 10% ethanol in benzene solution which contained 0.2 g. of phenyl β-naphthylamine. To this mixture was added 300 ml. of benzene, and the resulting suspension was allowed to stand with occasional stirring for about twenty-four hours. At the end of this time, solution was virtually complete, and the insoluble gel present was removed by filtration through a wire screen. The filtrate was added in a fine stream to 1 liter of a rapidly stirred solution of 0.2% phenyl β-naphthylamine in methanol. The precipitated polymer was washed with 200 ml. of 0.2% phenyl β-naphthylamine in methanol and finally dried at 80° for five hours under a reduced pressure of less than 1 mm.

The polymer contained in the second polymerization bottle was used as the control sample. After the twenty-one hour polymerization period at 30°, which was followed by cooling of the reaction mixture at 0°, the bottle was opened. The excess sodium was destroyed with a 10% solution of ethanol in benzene. The polymer was purified and isolated in exactly the fashion described in the previous paragraph for the heated polymer.

The products obtained above were analyzed by perbenzoic acid titration[4] for external double bonds. The analytical values obtained are expressed as per cent external double bonds as follows: control polymer, polymerized for twenty-one hours at 30°, 66.1%; polymer, heated to 100° for five hours after polymerization period of twenty-one hours at 30°, 65.8%.

NOYES CHEMICAL LABORATORY
UNIVERSITY OF ILLINOIS
URBANA, ILLINOIS

RECEIVED NOVEMBER 4, 1948

---

[4] Kolthoff and Lee, *J. Polymer Sci.*, **2**, 206 (1947).

[5] NOTE ADDED IN PROOF: See Robertson and Marion, *Can. J. Research*, **26B**, 657 (1948).

[6] The sample of sodium-polymerized polybutadiene used had been prepared by Dr. Bailey at the University of Illinois Laboratories in connection with the Government Synthetic Rubber Program.

[7] Marvel, Bailey and Inskeep, *J. Polymer Sci.*, **1**, 275 (1946).