after which it melts at 218–221°. A sample was crystallized by extraction in a Soxhlet apparatus with ether; a fine, white powder melting at 220° was obtained. A known sample of tetraphenyl-ethylene melted at 221° and the mixed melting point was 218°.

In conclusion the authors take pleasure in acknowledging their deep obligation to Dr. Henry Gilman of Iowa State College for the friendly way in which he has aided them in preparing this paper for publication, giving freely of his extensive knowledge and understanding of Grignard reactions.

Further studies are being made by one of us (W. L. G.) under a grant from the National Research Council.

Summary

Carbon monoxide has been made reactive with Grignard reagents, but only as a constituent of nickel carbonyl. The nickel carbonyl is, however, continuously regenerated from the liberated nickel and fresh carbon monoxide.

With phenylmagnesium bromide as the reagent the identified products are triphenylmethane, triphenyl-vinyl alcohol, pentaphenylethane and tetraphenyl-ethylene. Reactions for the formation of these compounds have been formulated on the assumption of a structure $Ni(=C=O)_4$, the double bond $Ni=C$ being the first point of attack, both the MgBr and C_6H_5 groups adding to the carbon atom. The $C=O$ double bond may still be attacked in the normal way and the new C—MgBr grouping is capable of reacting as a new Grignard reagent, thus giving a great number of possible substances, a mixture of which is probably contained in the non-crystallizable oil which comprises rather more than one-half of the entire product.

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[CONTRIBUTION FROM THE JESSE METCALF CHEMICAL LABORATORY OF BROWN UNIVERSITY]

A STUDY OF THE PREPARATION OF QUINIZARIN[1]

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Introduction

Quinizarin, or 1,4-dihydroxy-anthraquinone, is an important dye intermediate. The substance has been made by many methods[2] but there

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[1] Abstract of a thesis submitted to the Faculty of the Graduate School of Brown University in partial fulfilment of the requirements for the Degree of Master of Science.

[2] (a) Grimm, *Ber.*, **6**, 506 (1873). (b) Baeyer and Caro, *Ber.*, **8**, 152 (1875). (c) Liebermann, *Ann.*, **212**, 11 (1882). (d) Wacker, *J. prakt. Chem.*, [2] **54**, 90 (1896). (e) Friedländer, "Die Fortschritte der Teerfarbenfabrikation," **4**, 296 (1895); Ger. pat., 81,245; **4**, 301 (1896); Ger. pat., 86,630; **4**, 274 (1895); Ger. pat., 81,960; 11, 588 (1912); Ger. pat., 255,031.

seems to be no published study of the influence of progressively varying conditions upon the quantity and quality of the product obtained. This has led the writers to undertake such an investigation, of which the following paper is an account.

The method of preparation selected for study[3] consists essentially in heating together *p*-chlorophenol, phthalic anhydride, boric acid and sulfuric acid. A yield of 70–80% of crude product is claimed in the patent literature. No method of purification is given.

Experimental Part

The experimental results of varying the different factors involved in the reaction are collected in Table I.

TABLE I

PERCENTAGE YIELDS OF QUINIZARIN UNDER VARIOUS CONDITIONS OF OPERATION

p-Chlorophenol, 11.5 g.; phthalic anhydride, 40 g.; 96% sulfuric acid, 200 g.

INFLUENCE OF TIME

Boric acid, 10 g.; max. temp., 190°

Total time, hrs.	6	7	8	9	10	11	13
Yield, %	54.5	54.1	53.6	59.7	62.0	65.2[a]	69.0[a]

INFLUENCE OF BORIC ACID

Max. temp., 190°; total time, six hrs.

Boric acid, g.	0	2.5	5	10	15
Yield, %	48.2[b]	53.7[a]	65.2	54.5	56.9

INFLUENCE OF TEMPERATURE

Boric acid, 5 g.; total time, four hrs.

Max. temp., °C.	190	200	210	220	220	220
Yield, %	64.8	74.0	75.5[a]	69.8[b]	72.7[c]	72.7[d]

[a] Less pure; [b] impure; [c] time, 2.5 hrs., impure; [d] time, 2.5 hrs., boric acid, 10 g., impure.

The yields in all cases are calculated upon the basis of the *p*-chlorophenol employed in the reactions. The purity of the quinizarin was estimated by the following method. A small quantity of the product (1 to 2 mg.) was dissolved in a little pure acetone and allowed to crystallize slowly on a microscope slide. The crystals obtained were compared under the microscope with those of a standard of highly purified quinizarin treated in a like manner. The pure substance crystallizes in perfectly shaped, rectangular, orange plates, but products containing impurities crystallize either in irregularly shaped plates or shapeless masses. All the products listed in the table were very pure, except as specially indicated.

The results as shown appear to justify the following conclusions. 1. Increasing the time of reaction greatly has a favorable influence upon the yield but it is doubtful whether the small gain is worth the time consumed

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[3] Ger. pat., 255,031 (1912).

to obtain it. 2. The boric acid has a marked influence upon the reaction. Under the conditions of our experiments a quantity equal to 2.5% of the sulfuric acid used is distinctly the most favorable. 3. The optimum temperature for the reaction appears to be 200°. A lower temperature decreases the rate of reaction, while a higher one causes the formation of impurities, even though the time of reaction is simultaneously decreased, or the time decreased and the quantity of boric acid increased.

It was further found best to use a quantity of phthalic anhydride which is 227% of the calculated amount.

Large Scale Run

As a concluding experiment a run was made on a ten-fold scale in order to test the adaptability of the process to large-scale laboratory production. This run represents a combination of the most favorable conditions as determined by the foregoing series of experiments. Following is a detailed description of the procedure.

A mixture of 115 g. (0.9 mole) of *p*-chlorophenol, 300 g. (2.0 moles) of phthalic anhydride, 50 g. of crystallized boric acid and 2000 g. of 96% sulfuric acid was heated for 3.5 hours in a bottle with a loosely fitting glass stopper immersed to the neck in oil at 200°. This does not include the time required for the mixture to become heated, which should be from 30 to 45 minutes. The colored melt was poured into 5 liters of water and filtered. The precipitate was boiled with 10 liters of water and filtered hot, to remove the excess of phthalic anhydride. The residue was next suspended in 10 liters of boiling water, and to this suspension was added a sufficient quantity of 50% potassium hydroxide solution[4] to produce a purple color (about 30 cc.), followed by 300 cc. more. The alkaline solution was filtered hot, and the residue washed with 200 cc. of 2% potassium hydroxide solution and discarded. The filtrate was saturated with carbon dioxide and the precipitated quinizarin again filtered off. The product was then boiled with 5 liters of a 10% solution of sodium carbonate until it appeared black (monosodium salt?), to dissolve the last traces of purpurin. The mixture was cooled to room temperature, filtered, and the precipitate boiled with 5 liters of 5% hydrochloric acid to liberate the quinizarin. The product was then filtered off, washed and dried at 100°. It weighed 160 g. which is 74% of the calculated yield, sintered at approximately 190° and melted at 194–195° (uncorr.), or 199–200° (corr.). According to the literature, highly purified quinizarin melts at 194–195° (uncorr.).[5]

Summary

A study has been made of the influence of certain factors upon the yield and purity of product in the preparation of quinizarin from *p*-chlorophenol, phthalic anhydride, boric acid and concd. sulfuric acid. A method of preparation involving all the most favorable conditions is described in detail.

PROVIDENCE, RHODE ISLAND

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[4] x Grams of potassium hydroxide made up to 2x cc. of solution.

[5] Ref. 2 a, p. 508.