

above. In the phenolic fraction only guaiacol was identified. The "neutral" fraction on oxidation yielded an acid which was identified as anisic acid by its melting point, mixed melting point, and the optical properties of the crystals.

Summary

1. Alkali lignin, isolated from corn cobs, was distilled with zinc dust in an atmosphere of hydrogen at a maximum temperature of 400°. The oily distillate was separated into a phenolic fraction and a "neutral" fraction. In the phenolic fraction guaiacol and 1-*n*-propyl-3-methoxy-4-hydroxybenzene were identified. The "neutral fraction" when oxidized with potassium permanganate yielded anisic acid.

2. The significance of these findings from the standpoint of the structure of lignin is briefly discussed.

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[CONTRIBUTION FROM THE PRIVATE LABORATORY OF THE AUTHOR]

ALKYLATION OF ORANGE I. A REFUTATION

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Introduction

There has recently appeared a paper by K. H. Slotta and W. Franke,¹ entitled "Zur Konstitution der Azo-Indicatoren. I. Mitteilung: α -Naphthol-Orange" ("The Constitution of Azo Indicators. Part I. α -Naphthol Orange").

When the writer first glanced over this paper, he was struck by the novel character of it, and by the departure of the two authors from long established and often confirmed experience, concerning the constitution and certain typical properties of those azo dyes which carry a phenolic hydroxyl group in para position to the azo group. Such dyes have always been known to be very sensitive to the action of alkali, in so far as their usually yellow or orange shades are turned deep red, even by weak alkalies. It has been recognized long ago that the alkylation of the hydroxyl group renders these dyes indifferent, or to use the technical term, "fast" to alkali, and thereby makes them suitable for certain practical applications—for instance, the dyeing of textile goods.

Amongst the members of the group of azo dyes mentioned above, there is one called Alpha-Naphthol-Orange or Orange I, which is made by coupling diazotized sulfanilic acid with α -naphthol, and it is this particular dye with which the paper of Slotta and Franke deals.

It seems that relative to the alkylation of this dye, there is no reference in the chemical literature previous to the article of Slotta and Franke but

¹ Slotta and Franke, *Ber.*, **64**, 86 (1931).

there is not the least reason for presuming that this alkylation, if actually performed, should take a different course than the alkylation of other *p*-hydroxy azo dyes. The only difference which has in the past been noticed between various members of the group was the readiness with which alkylation takes place, but there has never been any doubt as to the spot which is attacked. Slotta and Franke, however, make the startling claim that the alkylation of Orange I does not produce phenolic ethers as usual but that the alkyl group becomes attached to one of the two nitrogen atoms of the azo group, and that consequently the mono alkyl derivatives of Orange I are turned red by alkali, just as Orange I itself. This claim rests on the results of some alkylation experiments which Slotta and Franke have made. They consider their interpretation of these results as a solid support of their claim although they admit that they have failed in their attempts to furnish positive experimental proof of the alkyl-nitrogen attachment. The ultimate object of the work of Slotta and Franke is the promotion of a new physico-chemical theory on the relations between indicator properties and constitution of azo dyes. For the details the reader should consult the original paper. Slotta and Franke have possibly not been aware of the sensational character of the claim derived from their alkylation experiments. It amounts to no less than the discovery of a reaction which is without parallel in the chemistry of the azo dyes, and which is contrary to fundamental conceptions of the organic dyestuff chemist. Before the latter submits to the painful process of giving up these conceptions, he will, of course, investigate the validity of the experimental proof furnished by Slotta and Franke.

This was the object of the writer in making the experiments described in the following pages.

Experimental

The occasion demands that in the description of his basic experiments the writer must go into more detail than would ordinarily be necessary. Slotta and Franke give a rather meager account of the synthetic part of their work, while they devote more space to their physico-chemical tests and theoretical deductions.

Methylation of Orange I.—Slotta and Franke used only 3.3 g. of starting material for their experiment. Such an amount is rather small for this type of research, unless the investigator is certain that the reaction will take the expected course and that it will be quantitative. No such certainty existed in the case at hand. Furthermore, Slotta and Franke have worked up the reaction mass with acid, which is impractical and deceiving, as will be seen. In the following three experiments the amounts used by Slotta and Franke were multiplied by five and the reaction mass was worked up alkaline, whereas relative proportions of the reacting materials and the reaction time were exactly the same as in Slotta and Franke's experiment.²

² Ref. 1, p. 90.

Experiment I.—Slotta and Franke state that they have heated the reaction mixture on the water-bath but they do not record the temperature which the mass has reached. It was assumed to have been 50 to 60° because they mention this temperature in the description of another experiment on the same page.

16.5 g. (one-twentieth mole) of Orange I, free acid,³ was put into a 250-cc. round-bottomed flask; 60 cc. of water was added and 12.5 cc. (three-twentieth mole) of caustic soda solution, 40° Bé. A deep cherry red solution resulted. To this was added within five minutes under constant shaking 15 cc. (three-twentieth mole) of dimethyl sulfate⁴ in three portions. Shaking was kept up another five minutes. The mixture became thicker and slightly warm. It was then heated on the water-bath for one hour so that a thermometer inserted into the flask content registered a temperature of 50 to 60°. The mass had then assumed an acid reaction, as was to be expected. It was dissolved with a mixture of 150 cc. of water and 23 cc. caustic soda solution of 40° Bé. The resulting solution was deep cherry red, exactly like the original alkaline solution of Orange I. However, a close inspection revealed a fine suspension in the liquid. This was filtered on a Buchner funnel and the cake was washed with distilled water until the filtrate was no longer deep red but merely pale orange. The filter cake, after drying in the air, weighed 10.5 g.⁵ When dissolved with 150 cc. of boiling water, a glittering mass of fine crystals separated out on standing. The microscope disclosed a uniform array of pale yellow boat-shaped individuals. These were filtered off and dried in the air, giving 8.8 g. of substance of a pronounced micro-crystalline structure, light orange in color with a distinct brownish-golden bronze.

This material⁶ differs radically from the sodium salt of Orange I. It is moderately soluble in cold water and its shade (yellow in dilute solution) is not in the least changed by weak or strong alkalis (spot test on filter paper). It has, therefore, no indicator properties whatsoever.

This behavior shows convincingly that the methylation has taken the normal course and that the methyl ether of Orange I has been formed, just as such ethers are formed in analogous cases.

Anal. 3.1630 g. of the air-dried material weighed 2.8741 g. after heating for two hours at 120°. This loss is equivalent to two molecules of water of crystallization. Subs. (anhydrous), 0.4692: 12.6 cc. of 0.2 *N* HCl. Calcd. for $C_{17}H_{18}O_4N_2SNa$: N, 7.69. Found: N, 7.55.

For the nitrogen determination the Phelps-Daudt modification of the Kjeldahl method was used.⁷

A sharp line of discrimination between the sodium salt of Orange I and its methyl ether is drawn by the following qualities. In dilute (*e. g.*, 2%) caustic soda solution,

³ It is much more convenient to use 20 g. (one-twentieth of a mole) of Orange I Food Color (which contains 90% pure coloring matter in the form of the sodium salt) and consequently 8.3 cc. (two-twentieth of a mole) of caustic soda, 40° Bé. This was done in the following experiments.

⁴ From Eastman Kodak Company.

⁵ From the deep red filtrate an excess of concentrated hydrochloric acid precipitated tiny black needles, just as did the original solution of Orange I.

⁶ It is, of course, a sodium salt since it has separated out of a sodium hydroxide solution.

⁷ The method was found very reliable. It is hard to understand why most scientific research laboratories still persist in using the antiquated and cumbersome Dumas method after so elegant a method as that of Phelps and Daudt has become available (see *J. Assn. Off. Agr. Chem.*, **3**, 310 (1920)).

Orange I is very readily soluble (deep red) while the ether is very nearly insoluble (filtrate practically colorless).

Another feature of the ether we will meet with in the following experiment.

Experiment 2.—This experiment was made in order to determine whether heating of the reaction mass on the *boiling* water-bath made any difference in the result. The experiment has led to an interesting observation.

The procedure was exactly the same as in Expt. 1 except that the thermometer in the reaction flask registered a temperature of about 90° against 50 to 60° in Expt. 1. No methyl ether could be isolated in this case.

The cause was discovered when a little sample of the pure methyl ether from Expt. 1 was boiled in a test-tube with dilute (10%) sulfuric acid. The resulting solution was turned red by alkali just as was the solution of Orange I. The acid had obviously hydrolyzed the ether.

This instability of the ether in an acid medium, especially at a higher temperature, explains why no ether was obtained in Expt. 2.

Experiment 3.—Experiment 2 has shown the importance of the temperature in regard to ether yield. Therefore Experiment 3 was made without application of heat in order to see whether this procedure would increase the yield over that of Experiment 1. This was found to be the case: 12.9 g. of crude⁸ ether was obtained equal to 65% of the theoretical yield, against 53% in Experiment 1.

Ethylation of Orange I.—In their ethylation experiment⁹ Slotta and Franke have boiled Orange I under reflux in alcoholic solution with caustic soda and diethyl sulfate. Their experiment was repeated and no ether whatsoever could be isolated. This result corresponds to that of methylation Experiment 2 described above. Then another experiment was made exactly analogous to the writer's methylation Experiment 3 merely substituting the equivalent amount of diethyl sulfate for the dimethyl sulfate. 10.3 g. of air-dry ether was obtained. This is a yield of about 50% of the theoretical. This material was crystallized from 200 cc. of water and yielded 7.8 g. of air-dry substance.

Anal. 5.1940 g. after heating for two hours at 120° weighed 4.7428 g. This loss is equivalent to two molecules water of crystallization. Subs. (anhydrous) 0.3693: 9.7 cc. of 0.2 *N* HCl. Calcd. for $C_{18}H_{15}O_4N_2SNa$: N, 7.41. Found: N, 7.38.

The ethyl ether formed a coarsely crystalline powder without brownish bronze and, therefore, of a brighter orange appearance than the methyl ether. Otherwise its properties are so similar to those of the methyl ether that they need not be especially described.

The rest of the alkylations we can deal with more briefly because the results were perfectly analogous, as was to be expected.

Propylation and Butylation of Orange I.—The method employed by Slotta and Franke was used, that is, boiling in alkaline alcoholic solution with *n*-propyl-*p*-toluenesulfonate or *n*-butyl-*p*-toluenesulfonate. For the sake of uniformity sodium hydroxide was substituted for the potassium hydroxide used by Slotta and Franke¹⁰ and the reaction mass was, of course, worked up alkaline after evaporation of the alcohol. The yields of crude ether were about 57 and 65% of the theoretical, respectively.

Hexylation of Orange I.—Again the same method as that of Slotta and Franke was used, namely, boiling in alkaline alcoholic solution with *n*-hexyl bromide. The ether yield was about 44% of the theoretical.

⁸ By "crude" is meant "not recrystallized" but the preparations were washed free from unchanged Orange I and from mineral salts.

⁹ Ref. 1, p. 91, No. 3.

¹⁰ Slotta and Franke use sodium hydroxide in some experiments and potassium hydroxide in others.

Résumé of the Experimental Work of the Writer and Interpretation of the Work of Slotta and Franke

The experiments described above have brought to light the facts in regard to the alkylation of Orange I when employing the methods of Slotta and Franke.

It has been found that the ethers of Orange I can be isolated to an extent of between 44 to 65% of the theoretical and that these ethers are stable to alkali but readily hydrolyzed by acids.

The alkaline filtrates from the ethers gave on precipitation with acid dark crystalline precipitates which displayed not a single feature which would warrant the conclusion that they represented anything else but starting material, that is, the free acid of Orange I.

The sensitiveness of the ethers of Orange I to acid is quite remarkable. Simple test-tube experiments give the following picture. While boiling with dilute mineral acid effects rapid hydrolysis of the ethers, a gradual hydrolysis takes place on mere standing with the acid and even with weak acids like acetic acid. It is, therefore, impossible to prepare the free color acids of the ethers in a pure state.

These facts put us now in a position to determine precisely what has taken place in the work of Slotta and Franke. Slotta and Franke have completely overlooked the formation of the ethers. They have treated the reaction mass of all their experiments with hydrochloric acid. They have, therefore, hydrolyzed the ethers which had been formed and finally they have had nothing in hand but more or less pure starting material.

Analytical evidence that acid treatment (even cold) of the reaction mass leads merely back to the starting material is furnished by the following experiment.

Experiment.—Butylation of Orange I, following the method used by Slotta and Franke in every respect (but multiplying the amounts by three), treatment with acid, thorough purification of the product and determination of the nitrogen.

The acid treatment and the purification were done without application of heat; 9.9 g. of free acid of Orange I was dissolved with 150 cc. of ethanol (92%) and 3.6 g.¹¹ of potassium hydroxide (sticks, by alcohol). Then 13.8 g. of *n*-butyl-*p*-toluenesulfonate was added. This solution was kept gently boiling on the water-bath under reflux for four hours. Then it was allowed to cool and was filtered on a Buchner funnel. The cake was pulped up in a mortar with 60 cc. of dilute (10%) sulfuric acid.¹² The pulp was then filtered and washed free from sulfuric acid with dilute hydrochloric acid. Then it was dissolved with ethanol and reprecipitated with hydrochloric acid. The material was filtered on the Buchner funnel, washed with ether, dried in a potassium hydroxide vacuum desiccator and then exposed to the air for a few hours; yield, 6 g.

¹¹ The figure of 0.2 g. in *Ber.*, p. 92 No. 4, 5 and 6 is a typographical error. It should read 1.2 g.

¹² It is always advisable to use sulfuric acid in order to liberate sulfonic acids from their salts, because there are examples in the literature when hydrochloric acid has done the work incompletely.

² Marvel and du Vigneaud, *THIS JOURNAL*, **46**, 2093 (1924).