Summary

1. In the Hofmann rearrangement, methyl chloride dissociates from the methylaniline hydrochloride and adds to a second molecule until trimethylphenylammonium chloride is formed, and this is the compound that rearranges.

2. No rearrangement takes place at 220–250° unless the heating is continued for 96 hours.

3. The rearrangement takes place at 300° and is somewhat affected by time; however, temperature is the main variable.

4. Neither methylaniline nor dimethylaniline rearranges.

5. A quantitative separation and determination of the three classes of amines have been developed incident to studying the rearrangement.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE UNIVERSITY OF NOTRE DAME]

THE CATALYTIC CONDENSATION OF ACETYLENE WITH PHENOLS

BY HERMAN H. WENZKE AND J. A. NIEUWLAND

RECEIVED OCTOBER 10, 1923

The condensation of acetylene with phenols was effected in 95% alcoholic solution and in the presence of concd. sulfuric acid and mercury salts. The proportion of alcohol used to dilute the phenolic compound varied, but a sufficient amount was used so that there would be no precipitation when sulfuric acid was added to the solution. The acid content of the reaction mixture was approximately 15 to 20%, but in cases where the absorption proceeded slowly the acid concentration was increased to 40%. As mercuric sulfate is only very slightly soluble in the reaction mixture, its concentration is of slight importance. Care was taken, however, to have it in slight excess. The acetylene was under a pressure of from 0.1 to 0.16 atmosphere, and a closed absorption system was used. The quantity of gas that had reacted was determined by the increase in weight of the reacting mixture. In these experiments the object was rather to investigate the products formed than to determine the intermediate compounds.

Phenol, under the conditions mentioned, absorbed acetylene very readily, but the product formed did not have the properties of the ethylidene diphenylol prepared from acetaldehyde and phenol.[1] The entire product formed was soluble in sodium hydroxide and various organic solvents but attempts to obtain crystals from these solutions met with failure. Very little information was obtained as to the constitution of the acetylene-phenol condensation products. The results with *ortho, meta*

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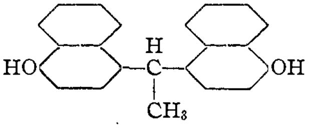
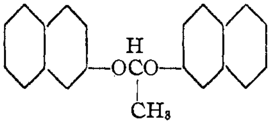
[1] Claus and Trainer, *Ber.*, **19**, 3009 (1886).

and *para* cresols were similar to that obtained with phenol. Glacial acetic acid solutions of phenol were also used. In the latter case a fusible resin resulted.[2]

Condensation with the Naphthols.—Alpha- and beta-naphthols were allowed to absorb acetylene under the conditions mentioned above. They were found to react differently. The principal product in the case of the β-naphthol was the acetal, while the entire product formed by the α-naphthol was soluble in alkalies. The reaction in the case of one molecule of acetylene with two of α-naphthol gives I, while that with β-naphthol gives II.

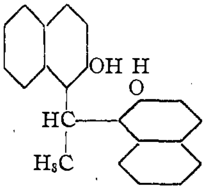


I

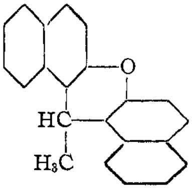


II

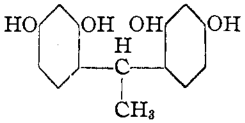
Beside the acetal, two other compounds were isolated from the acetylene-β-naphthol condensation, namely ethylidene di-β-naphthol (III) and ethylidene di-β-naphthyl oxide.



III



IV



V

Some of the ethylidene di-β-naphthol then liberated a molecule of water and formed an internal ether (IV). The formation of an acetal by the condensation of acetylene and β-naphthol showed that the latter has some of the properties of an alicyclic compound. No other phenol was observed to react in this way, while many aliphatic alcohols are known to condense with acetylene to form acetals.[3] The fact that α-naphthol did not form the acetal shows that the hydroxyl is in the aryl part of the naphthol molecule. The difference in the behavior of the two naphthols toward acetylene is an additional proof that there is a difference in the structure of the two rings of naphthalene, the substitution with α-naphthol being in the aryl ring and with β-naphthol in the alicyclic ring.

To a solution of 50 g. of β-naphthol in 150 cc. of alcohol was added 15 g. of concd. sulfuric acid and some mercuric oxide. The mixture was allowed to absorb acetylene for ten days. At the end of that time a considerable amount of solid material had settled out of the solution. The contents of the flask were poured into a beaker of water, then filtered, and the pre-

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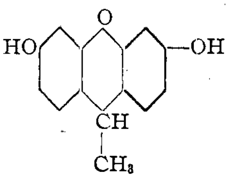
[2] Ellis, "Synthetic Resins and their Plastics," **1923.**

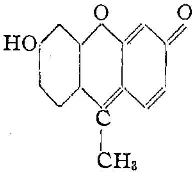
[3] Reichert, Bailey and Nieuwland, This Journal, **45,** 1553 (1923).

cipitate was washed thoroughly with hot water. The entire product was dissolved in benzene; the process of solution shows that it was not a single compound. By fractional crystallization from boiling benzene, one of the compounds was obtained in a pure condition. After the sixth crystallization the substance had a definite melting point, 168.5°. This compound was ethylidene di-β-naphthol. A second compound was obtained by treating part of the washed product with boiling 5 to 10% sodium hydroxide solution, and digesting the mixture three or four times with boiling alcohol. This treatment left a small amount of a colorless, crystalline compound melting at 173° and in general corresponding to the properties of ethylidene di-β-naphthyl oxide mentioned above and described in such handbooks of organic chemistry as that by Beilstein. The greater part of the reaction product, however, was the acetal.

The Reaction with Resorcinol and Hydroquinone.—An alcoholic solution of resorcinol in the presence of concd. sulfuric acid and mercuric oxide was allowed to absorb acetylene until the amount taken up was in the molecular ratio to resorcinol of one to two. The product formed was soluble in the reaction mixture and in water. It is believed, as will be shown later, that this product was ethylidene diresorcinol (V), the positions of linkage being *ortho* and *para*, respectively, to the two hydroxyl groups. No reference could be found in the literature regarding the properties of ethylidene diresorcinol, but this must be the initial product. When the reaction mixture is poured into water and let stand for a few hours the solution becomes somewhat colored and a precipitate begins to settle, showing that a chemical reaction has taken place in the aqueous solution. The formation of a substance insoluble in water from the original reaction mixture cannot be a process of oxidation as it proceeds even if the solution is placed in closed tubes. This reaction must be one of dehydration, one molecule of water being removed from compound V to give VI.



VI



VII

This compound, dihydroxy methylxanthene, is soluble in water, soluble in alkalies, and decomposes without melting at 230° to 240°.

When this dihydroxy-methylxanthene was heated in an oil-bath at a temperature of 160° to 180° in the presence of stannic chloride (crystals), it was oxidized to form a colored substance, hydroxymethylfluorone (VII), the solutions of which very closely resemble those of fluorescein. The formation of hydroxymethylfluorone showed that the assumption as to the course of the reaction with acetylene and resorcinol was correct. No ultimate analyses were made of either the naphthol or the resorcinol compounds, the identification being considered sufficiently conclusive without such data. Attempts to isolate ethylidene diresorcinol in a crystalline state failed. This seems strange from the fact that methylene diresorcinol is a solid that does not melt below 250°. Ethylidene diresorcinol is very soluble in water and when its solution was evaporated a viscous semi-solid was obtained. It might be mentioned here that this hydroxymethylfluorone was obtained by starting with aldehyde and resorcinol. It was not possible to crystallize ethylidene diresorcinol from the reaction mixture of aldehyde and resorcinol.

Acetylene and hydroquinone unite to form a substance entirely soluble in alkali but insoluble in water. This product polymerized on standing and further investigation was impossible.

The Polyhydroxy Benzenes.—The catalytic action of acetylene with these compounds was not investigated very far because of difficulties met in isolating the compounds and also on account of their instability. It was noted simply that pyrogallol and phloroglucinol reacted very readily with acetylene, that the reaction product is in both cases soluble in alkali, and that from pyrogallol is slightly soluble in water.

The Effect of Different Side Chains on the Reaction of Phenols with Acetylene.—*Ortho* and *para* nitrophenols, phenolsulfonic acid, and methyl salicylate do not react with acetylene. According to Crum Brown's rule, the groups already present (nitro, sulfonic acid, and carboxyl groups) should direct the entering group to the *meta* position. No case was noted where the ethylidene group occupied a position *meta* to a side chain. Instead of occupying a position *meta* to another group the acetylene does not react at all.

It was observed that the ether phenetol did not react with acetylene, the replacement of a hydrogen of the hydroxyl group of phenol by an ethyl group apparently preventing the reaction.

Summary

1. Phenol and the cresols condense with acetylene in the presence of catalytic agents but the product formed is a mixture from which it has been impossible to crystallize pure compounds.

2. Beta-naphthol condenses with acetylene to form an acetal although a certain amount of ethylidene di-β-naphthol is formed. With the α-naphthol no acetal is formed. This difference in the reaction of the two naphthols toward acetylene constitutes additional proof that there is a difference in structure between the two compounds. The hydroxyl group in the case of α-naphthol is present in the aryl ring, while in the case of the β-naphthol it is a hydrogen in the alicyclic ring that is substituted.

3. Resorcinol condensed with acetylene to form ethylidene diresorcinol with linkage *ortho* and *para*, respectively, to the two hydroxyl groups.
4. Ethylidene diresorcinol gives off a molecule of water to form a new compound, dihydroxy-methylxanthene, which was oxidized to form hydroxymethylfluorone.
5. The di- and trihydroxy benzenes react with acetylene even more readily than does phenol.
6. The presence of negative groups as the nitro and sulfonic groups prevents the absorption of acetylene by the phenolic compound. As these groups, according to Crum Brown's rule, direct the entering group to a *meta* position, it appears that acetylene instead of entering in a *meta* position does not react at all. No cases have been observed where the acetylene substitutes in a *meta* position to another group.
7. The substitution of the hydrogen of the hydroxyl group of phenol by an ethyl group prevents reaction with acetylene.

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NEW METHODS OF SPLITTING PYRIMIDINES. III. THE ACTION OF IODINE SOLUTION ON PYRIMIDINES[1]

BY LAWRENCE W. BASS[2] AND OSKAR BAUDISCH

RECEIVED OCTOBER 13, 1923

The discovery of the fact that the stable pyrimidine ring can be ruptured under mild conditions, such as moderate temperatures and in neutral or weakly alkaline solution, led to a search for other methods of producing this decomposition. The reagents which have already been applied are:[3] (1) ferrous sulfate plus sodium bicarbonate plus air; (2) sodium pentacyano-aquo-ferroate plus oxygen or air; (3) ferrous sulfate plus oxygen; (4) ferrous sulfate plus hydrogen peroxide.

The observation of Pauly and Gundermann[4] that indole is oxidized to indigo with a 40% yield by iodine solution in the presence of sodium bicarbonate, led us to a study of this reagent as a possible means of splitting pyrimidines. The investigation was attended by marked success, since we were able to split uracil, thymine, 5-ethyluracil, 4-methyluracil and cytosine into urea and other products.

In the case of thymine we were able to detect acetol, but no pyruvic

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[1] Presented at the New Haven meeting of the American Chemical Society, April, 1923.

[2] National Research Fellow in Chemistry.

[3] Johnson and Baudisch, (a) THIS JOURNAL, **43**, 2670 (1921); (b) Pfaltz and Baudisch, *ibid.*, **45**, 2972 (1923).

[4] Pauly and Gundermann, *Ber.*, **41**, 4002 (1908).