it decomposed without melting. It seemed, therefore, useless to examine it further for the present.

The other ethylidene compounds were prepared in a similar manner. Ethylidene-*bis-tert.*-butylbenzene was separated from the small amount of an oily impurity accompanying it in the distillate by solution with alcohol in which it was less soluble than the oil. It was recrystallized from 95% alcohol.

The boiling points of the new hydrocarbons prepared are given in the accompanying table.

Summary

1. Ethylidene hydrocarbons of the general formula $CH_3CH(C_6H_4R)_2$ have been prepared from acetylene in the presence of concentrated H_2SO_4 and HgO from the following benzene derivatives: propyl- and *iso*propylbenzenes, *n*-butylbenzene, *tert.*-butylbenzene, methylethylphenylmethane, methyl*iso*propylphenylmethane, diethylphenylmethane. These are all viscous, amber colored liquids of high boiling points, excepting ethylidene-*bis-tert.*-butylbenzene which is a white crystalline solid.

2. Tetrahydronaphthalene gives with acetylene ethylidene-*bis*-tetrahydronaphthalene and also a six-ringed compound in small quantities.

3. Polynuclear hydrocarbons such, for example, as diphenyl, diphenylmethane, dibenzyl, triphenylmethane and naphthalene do not react with acetylene.

Notre Dame, Indiana

[Contribution from the Research Laboratories, University of Notre Dame]

THE CATALYTIC CONDENSATION OF ACETYLENE WITH PHENOLS. II. RESORCINOL

By S. Aquinas Flood and J. A. Nieuwland

Received July 5, 1928 Published September 5, 1928

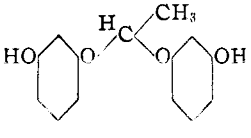
Introduction

In 1923 Wenzke and Nieuwland[1] reported the condensation of acetylene with resorcinol in the presence of sulfuric acid and mercury salts. The product was not separated from the alcoholic reaction mixture until it had undergone a dehydration. This second reaction was induced by diluting with water, whereupon a fine yellow precipitate slowly formed. On oxidation with stannic chloride this precipitate yielded hydroxymethylfluorone (II), indicating that the yellow compound was dihydroxymethylxanthene (IV). It was thought desirable, however, to make a more complete study of the reaction in an attempt to secure the primary product in the pure state, and to discover if this reaction resembled other acetylene reactions in giving the same products as acetaldehyde.

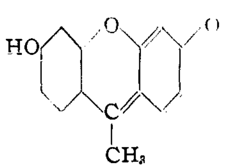
---

[1] Wenzke and Nieuwland, This Journal, **46**, 179 (1924).

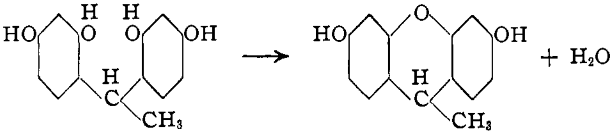
The literature on the reaction of acetaldehyde with resorcinol shows considerable difference of opinion. In 1894 Causse[2] reported the product as being the acetal of resorcinol (I), basing his conclusion largely on analysis and reaction of the diacetate. In the same year Möhlau and Koch[3] stated that resorcinol and aldehyde combined in different proportions at the same time—two moles of resorcinol to one of aldehyde, and two to two (one to one?). The oxidation of the first of these gave hydroxymethylfluorone (II), from which these investigators concluded that the aldehyde residue had been attached to nuclear carbons. Möhlau and Koch came to no conclusion regarding the constitution of the second resorcinol aldehyde compound.



I



II



III IV

In 1900 Fosse and Ettlinger[4] attempted to make the acetal of resorcinol by the action of ethylidene chloride on the potassium salt of resorcinol. They found that while their product seemed to be identical with that of Causse, it could not be "saponified" with sulfuric acid as other acetals could be. They concluded that some rearrangement had taken place, that the ethylidene group had become attached to nuclear carbons and that elimination of water had taken place giving dihydroxymethylxanthene (IV). They likewise secured a crystalline acetate which gave practically the same analysis as that of Causse.

Comparison of the products as described and of the methods of procedure shows that while Möhlau and Koch secured a white, microscopically crystalline product from acetaldehyde and resorcinol in aqueous solution acidified with hydrochloric acid, Causse and Fosse and Ettlinger describe their products as being yellow, although the former did the aldehyde condensation in dilute sulfuric acid and the latter heated the ethylidine chloride, aqueous potassium hydroxide and resorcinol in a sealed tube.

---

[2] Causse, *Ann. chim.*, **1**, 96 (1894).

[3] Möhlau and Koch, *Ber.*, **27**, 2891 (1894).

[4] Fosse and Ettlinger, *Bull. soc. chim.*, **23**, 518 (1900).

Nieuwland[5] used ethyl alcohol acidified with sulfuric acid as a solvent for the resorcinol and aldehyde mixture, which on the addition of water slowly precipitated a yellow substance, identical with that obtained from acetylene reactions.

Many solvents for the acetylene reaction mixture were tried in an effort to secure the primary product in a definitely crystalline form. Methyl alcohol finally was found to give the desired result.

Experimental

Fifty-five grams of resorcinol was dissolved in 400 cc. of methyl alcohol to which the mercury catalyst had been added. After the flask had been tared, washed and dried acetylene was passed in from a gasometer until 13 g. had been absorbed. The solution, originally almost colorless, became reddish brown, while the catalyst darkened and settled on standing. The liquid was decanted from the catalyst and its volume reduced about one-third by evaporation on a water-bath. The flask was tightly stoppered to prevent access of air, cooled and allowed to stand for several hours. In a short time white, needle-like crystals formed in considerable quantity. They were collected on a filter, washed with methyl alcohol and dried at room temperature in the air or in a vacuum desiccator. In some cases it was necessary to recrystallize from hot methyl alcohol in order to remove the last traces of the catalyst. The filtrate and washings were processed a second and a third time, after which they were diluted with water until a slight cloudiness showed and were then allowed to stand. Microscopic yellow crystals slowly precipitated. An average yield was 70 g. of the white compound (83%) and 6 g. of the yellow (10%). These yields are calculated for the formulas given below.

Discussion

Under the procedure described above the large quantity of the white compound seemed to indicate that it was the primary product. It decomposed without melting above 250°. A loss of weight was observed when the air dried crystals were heated in a current of carbon dioxide or under reduced pressure. The loss of weight was found to be constant in various samples between 18.3 and 18.8%. The evolved vapor was condensed and proved to be methyl alcohol. This indicated that alcohol of crystallization was present. Samples dried in a vacuum desiccator showed a lower, and more variable, percentage loss under similar treatment. When fresh, the crystalline product was only moderately soluble in cold alcohol, but very soluble in hot. It dissolved readily in sodium hydroxide solution with deep red coloration. In water, ether, benzene and petroleum ether it showed little solubility. The compound, however, after standing some days, became markedly less soluble even in hot alcohol. Corresponding to this loss of solubility there had been a great increase in molecular weight, as shown by determinations made at intervals of a few days. This change, apparently polymerization, took place even when the sub-

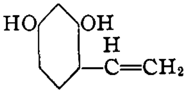
---

[5] Unpublished work, 1925. Read at Organic Section meeting, American Chemical Society at Los Angeles.

stance had been kept in sealed tubes, but was more rapid in the light. The crystals readily crumbled to a powder and if exposed to the air slowly became a yellowish brown. It was necessary to use fresh, air-dried crystals for the determination of the molecular weight as by the time the sample had been perfectly dried it had polymerized to such an extent as to be useless for examination. Samples of the same type were used for combustions.

Anal. Calcd. for $C_8H_8O_2 \cdot CH_3OH$: C, 64.25; H, 7.19. Found: C, 64.37; H, 6.96. Loss of weight on heating. Calcd.: 19.04. Found: 18.3, 18.8. *Mol. wt.* (Ebullioscopic in methyl alcohol). Calcd.: 168. Found: 169.

These results would seem to justify at least a tentative acceptance of formula (V) for this product, vinylresorcinol.



V

The polymerization of vinylresorcinol (V) is analogous to the behavior of cinnamic acid, vinylphenol and vinylcatechol, this latter compound never having been secured in the monomolecular form as far as the literature shows.

One of the great experimental difficulties encountered in the beginning of this investigation was the readiness with which the reaction mixture solidified to a crumbly, gelatinous mass insoluble in all ordinary solvents. This took place only when an excess of acetylene had been absorbed and was always accompanied by the odor of either dimethyl or diethyl acetal, according to the alcohol used as solvent. It did not occur in the case of other solvents. In order to test the assumption that the formation of this Bakelite-like mass was due to an acetal reaction, acetal was added to an alcoholic solution of resorcinol. No reaction took place until a small quantity of acid had been added, when the action became almost violent, with the formation of a clear, brittle, insoluble Bakelite closely resembling that formed in the acetylene reaction flask.

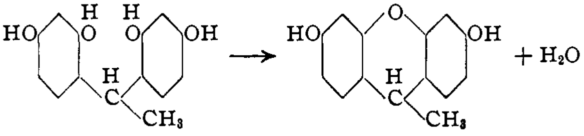
There is still doubt as to whether the yellow product has been secured in a pure state, free from vinylresorcinol. Its insolubility in water, however, and its oxidation to hydroxymethylfluorone (II) show that dihydroxymethylxanthene (IV) is present at least in considerable proportion. It is readily soluble in alcohol and ether as well as in alkali solutions and shows no tendency to polymerize.

Accordingly, the course of the acetylene–resorcinol condensation would seem to be as follows:

$$HC\equiv CH + (HO)_2C_6H_4 \longrightarrow \underset{(V)}{(HO)_2C_6H_3CH{=}CH_2}$$

$(HO)_2C_6H_3CH{=}CH_2 + (HO)_2C_6H_4 \rightleftharpoons$

V



III IV

This assumes (1) the formation of an intermediate product, ethylidenediresorcinol (III), which has not been isolated, and (2) a reaction between vinylresorcinol (V) and resorcinol. To test this latter assumption, alcoholic solutions of these compounds were mixed. At first practically colorless, the mixture soon turned reddish brown and, on dilution with water, precipitated the yellow compound (IV). Moreover, according to the reaction given above, equilibrium conditions would demand a larger amount of vinylresorcinol (V) in dilute than in concentrated solutions. This, too, was verified experimentally, the more dilute reaction mixtures always giving the higher yield of vinylresorcinol (V).

Derivatives

A. Methyl Ethers.—Attempts have been made to prepare the methyl ethers of vinylresorcinol (V) directly, but have thus far been unsuccessful. In fact, no reaction of vinylresorcinol in basic solution has been entirely satisfactory. It is probable that the base induces some sort of molecular rearrangement which is not reversible, but this point is still being investigated. Consequently the methyl ethers of resorcinol were prepared and their acetylene condensation products investigated.

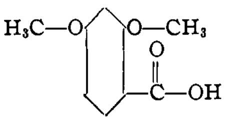
Experimental

One hundred ten grams of resorcinol was dissolved in 500 cc. of methyl alcohol, and then 46 g. of sodium gradually added, the reaction flask being kept under a reflux and frequently agitated. The solution was refluxed on a water-bath for an hour following the addition of the sodium, after which 252 g. of dimethyl sulfate was allowed to drop in slowly from a dropping funnel in the top of the condenser. It was necessary to cool the reaction flask during the addition of the first part of the dimethyl sulfate, and at the end to heat it on a water-bath. After an hour's heating, a sloution of 10 g. of sodium hydroxide was added in order to decompose the dimethyl sulfate completely and the heating was continued for another half hour. The flask was then cooled, the reaction mixture acidified and the methyl alcohol distilled off on a water-bath. Sufficient water to dissolve the salt was then added and the resorcinol ethers were extracted with ether. The ethereal solution was treated with 10% sodium hydroxide solution, which dissolved the monomethyl ether and permitted separation from the dimethyl compound. The solvent ether was distilled from the dimethyl ether of resorcinol and this latter distilled. It is a clear, oily liquid boiling at 210°. The caustic solution of the monomethyl ether was acidified, extracted with ether and then treated in the same manner.

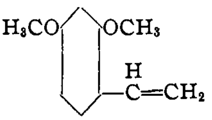
The resorcinol ethers were each dissolved in methyl alcohol and allowed to react with an equimolar quantity of acetylene in presence of the catalyst, as was resorcinol.

From the monomethyl ether only amorphous orange powders have been secured. The variable melting point and the lack of definite crystalline form would seem to indicate that the product is a mixture. Since side chain attachment to nuclear carbons of the monomethyl ether offers considerable opportunity for isomer formation, the condition described above was to have been expected, but not in the case of acetal linkage. Moreover, the complete solubility of the product in dilute alkali gave evidence that the hydroxyl group was still free.

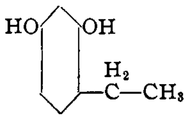
From the dimethyl ether a pale yellow oil boiling with decomposition at 235° was formed. This was oxidized by boiling with dilute nitric acid and also with dilute potassium permanganate. In both cases beautiful monoclinic crystals were formed from a hot water solution. The compound proved to be a monobasic acid melting sharply at 108°. It was identified as the dimethyl ether of β-resorcylic acid (VI); therefore the acetylene condensation product was undoubtedly the dimethyl ether of vinylresorcinol (VII). This is a further corroboration of previous experience that the side chain is attached ortho and para, respectively, to the hydroxyl groups, whether these be free or substituted.



VI



VII



VIII

B. **Ethyl Resorcinol.**—Owing to the slight solubility of vinylresorcinol and to its rapid polymerization, considerable difficulty was experienced in reducing it. The best results were obtained from the use of tin and hydrochloric acid. The product was extracted with ether, which was then evaporated. The residue was recrystallized from boiling benzene in the form of rather large prismatic crystals, melting at 98.5–99°. This product was identified as ethylresorcinol[6] (VIII). Its synthesis from vinylresorcinol is additional evidence of the correctness of the formula assigned to this compound.

C. **Acetate.**—When acetic anhydride in excess was added to vinylresorcinol (V), solution took place accompanied by evolution of heat. On standing, after refluxing about an hour, large rhombic crystals (m. p. 285–286°) slowly formed in the somewhat reddish solution. The product was identical in all respects with that of Causse and Fosse and Ettlinger, while the percentage yield was invariably high. Naturally there is no evidence of free hydroxyls, but in view of the synthesis from vinylresorcinol (V) this cannot be taken as evidence of acetal linkage of the side chain as Causse argues. The empirical formula he assigns to it, $C_{18}H_{18}O_6$, as the diacetate of the acetal (IX), gives the same percentage composition as that of the diacetate of vinylresorcinol (X), $C_{12}H_{12}O_4$, so there is no contradiction from analysis.

$$H_3CCOOC_6H_4—O—CH(CH_3)—O—C_6H_4—O—COCH_3$$

IX

$$(H_3C—CO—O)_2=C_6H_3CH=CH_2$$

X

Aldehyde Condensation

In order to duplicate as nearly as possible the conditions under which vinylresorcinol (V) had been made from acetylene, the aldehyde condensation was tried in methyl alcohol according to the following procedure.

[6] Johnson and Hodge, THIS JOURNAL, 35, 1020 (1913).

Experimental

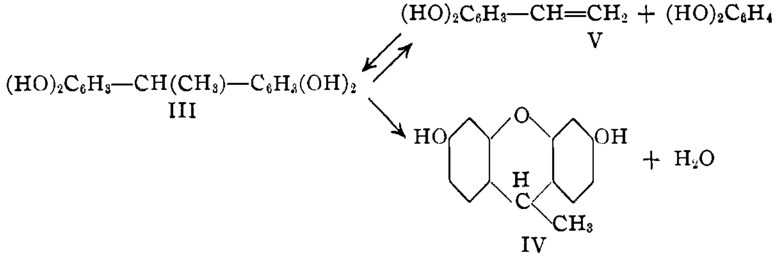
Twelve grams of dry hydrogen chloride was dissolved in 400 cc. of methyl alcohol and 110 g. of resorcinol added; 44 g. of paraldehyde was gradually added to this mixture during the two or three hours it was refluxed on a water-bath. The solution resembled the acetylene reaction mixture in all respects and on partial evaporation a copious precipitate of white, needle-like crystals formed exactly as in the acetylene reaction. Moreover, the filtrate from the third fractional crystallization gave the yellow compound (dihydroxymethylxanthene) on standing after dilution with water. Molecular weight determinations gave results agreeing with those obtained from the acetylene product, while all other properties and reactions of the white product seemed to be identical with those of vinylresorcinol (V).

Attempted oxidations of vinylresorcinol (V) from acetylene or from aldehyde have invariably failed to produce anything which gave even a trace of fluorescence, but the yellow secondary product on heating with stannic chloride gave the highly fluorescent hydroxymethylfluorone (II).

Discussion

There is little doubt but that the condensation of acetylene with resorcinol and the condensation of aldehyde with resorcinol give the same products. However, it is not as clear as to how the aldehyde reaction takes place as it is in the case of the acetylene reaction. The following equation seems the more plausible explanation.

$$2(HO)_2C_6H_4 + CH_3CHO \longrightarrow \underset{\text{III}}{(HO)_2C_6H_3—CH(CH_3)—C_6H_3(OH)_2} + H_2O$$



Schou,[7] however, has recently reported the presence of vinyl alcohol to the extent of $^1/_{830}$ in paraldehyde in the presence of hydrochloric acid and consequently vinylresorcinol may be formed immediately by the reaction of resorcinol with the enolized aldehyde.

Repetitions of Fosse and Ettlinger's ethylidene chloride experiments have been rather unsatisfactory. The reaction was tried in a sealed tube heated to the temperature given by these investigators, and also to much higher temperatures, but in both cases the ethylidene chloride reacted to so small an extent as to make the separation of the small quantity of product almost an impossibility. Yields proved to be equally unsatisfactory when the interacting substances were dissolved in methyl alcohol and refluxed for several hours.

---

[7] Schou, *Compt. rend.*, **184**, 1452 (1927).

The probable explanation of the differences of opinion expressed in the literature is that suggested by Möhlau and Koch: that the products reported have been mixtures of the products of condensation in different proportions. In this case derivatives would exhibit different properties according as the reaction with vinylresorcinol (V) or that with ethylidenediresorcinol (III) (dihydroxymethylxanthene (IV)) had predominated.

Summary

1. The primary product of the catalytic condensation of acetylene and resorcinol has been secured in crystalline form and identified as vinylresorcinol (V).
2. The dimethyl ether of vinylresorcinol (VII) has been shown to give the dimethyl ether of β-resorcylic acid on oxidation.
3. Reduction of vinylresorcinol has been effected, the product being ethylresorcinol (VIII).
4. The primary product of the condensation of aldehyde and resorcinol has been shown to be vinylresorcinol (V).
5. The work of previous investigators who showed the presence of dihydroxymethylxanthene (IV) in the products has been corroborated.
6. No evidence whatsoever in support of Causse's acetal formula (I) has been found, but a number of facts which argue against it have been observed.

NOTRE DAME, INDIANA

[CONTRIBUTION FROM THE LABORATORIES OF PHYSICAL CHEMISTRY AND AGRICULTURAL CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

THE QUANTITATIVE STUDY OF THE PHOTOCHEMICAL ACTIVATION OF STEROLS IN THE CURE OF RICKETS. II

BY STANISLAW-KAZIMIERZ KON, FARRINGTON DANIELS AND HARRY STEENBOCK

RECEIVED JULY 18, 1928 PUBLISHED SEPTEMBER 5, 1928

In an earlier paper from these Laboratories,[1] there were described experiments in which cholesterol was exposed to monochromatic light to determine the minimum number of quanta necessary to secure its antirachitic activation. This work was confined to the use of the 265 m. μ line of the mercury arc. It was followed by an extensive research by Dr. Waldemar Vanselow in which all the important lines of the quartz mercury lamp were studied under a wide variety of conditions.[2] As recent researches from several laboratories have indicated that it is ergosterol rather than cholesterol itself which produces the vitamin D upon irradiation, it seemed desirable to repeat and amplify the experiments, using ergosterol instead of cholesterol.

---

[1] Fosbinder, Daniels and Steenbock, THIS JOURNAL, **50**, 923 (1928).

[2] Unpublished data.