(calculated on the quantity of lignin used), 52.2%; gas, 13.5% (by difference); acetone, 0.13%; methanol, 1.9%; water-soluble acids (calculated as acetic acid), 0.05%. The oily distillate analyzed as follows: (The results are expressed as per cent. by weight of the oil) acids, 8.6%; phenols (fraction soluble in 5% KOH solution and insoluble in 5% $NaHCO_3$ solution), 84.0%, hydrocarbons and neutral compounds, 7.2%. In the phenolic portion of the oil guaiacol and eugenol were identified.

In the case of the Willstätter lignin and the lignin prepared by the 72% sulfuric acid method, the percentage of aqueous distillate was about the same as that obtained from alkali lignin, whereas the oily distillate was only about one-half. The percentages of carbon residues obtained from the Willstätter lignin and from the 72% sulfuric acid lignin were considerably greater than that obtained from alkali lignin. The percentages of acetone and acetic acid obtained were considerably greater in the case of the Willstätter and the 72% sulfuric acid lignin than in the alkali lignin, whereas, the percentage of methanol was less. This higher percentage of methanol is probably due, in part, to the greater methoxyl content of alkali lignin than that of Willstätter and 72% sulfuric acid lignin. A possible explanation for the lower yield of acetic acid obtained from alkali lignin is presented.

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NEW CONDENSATIONS OF KETONES WITH PHENOLS. III. CONDENSATION PRODUCTS OF MESITYL OXIDE AND MONOHYDROXYBENZENES

BY JOSEPH B. NIEDERL[1]

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Introduction

In continuation of the studies of the condensation possibilities of ketones with phenols, as begun with the condensation system phorone–cresols,[2] the condensation systems of mesityl oxide with monohydroxybenzenes were investigated. The discussion of the results of these investigations is the purpose of this communication.

Theoretical Part

By treating a molar mixture of mesityl oxide and a monohydroxybenzene with concentrated sulfuric acid in the cold, condensation products are ob-

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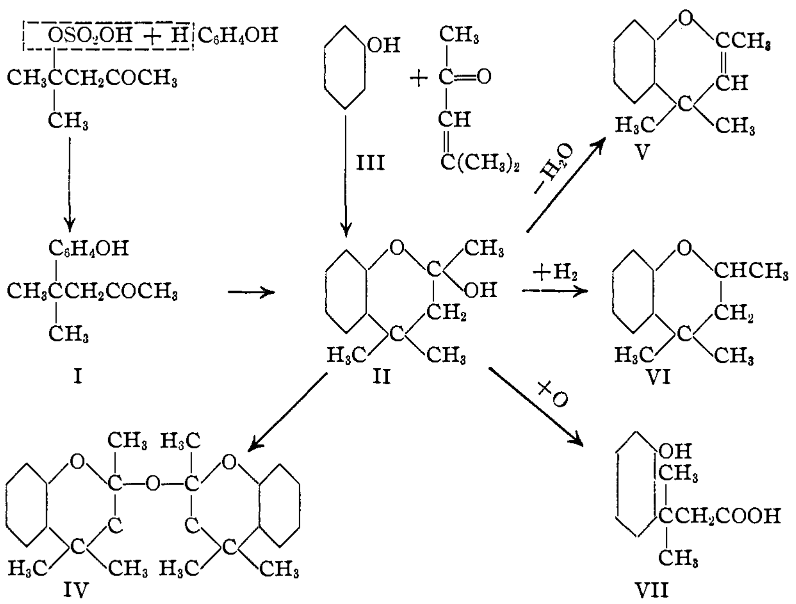
[1] In collaboration with Nathan Ambinder, Richard Casty, De Witt C. Knowles, Irving Rappaport and William Saschek.

[2] Niederl, THIS JOURNAL, **50**, 2230 (1928); Niederl and Casty, *Monatsh.*, **51**, 1028 (1929).

tained which appear to be chromanols (II) and dichromanyl ethers (IV) and their formation may be interpreted either (as illustrated in the chart) that from the mesityl oxide sulfuric acid (I) the phenyl-substituted isobutyl methyl ketone (I) is formed, which then changes into the isomeric chromanol (II), a behavior which is in harmony with observations made on structurally related substances,[3] or that their formation may have taken place in the form of a direct addition (III). In most cases, however, the reaction did not end with the formation of the chromanols, but dehydration occurred and the dichromanyl ethers (IV) resulted.

Both the chromanols (II) (they are really semi-acetals) and the dichromanyl ethers (IV) (di-acetals) are very stable toward alkali but are quite sensitive toward acids, as indicated by the formation of colored decomposition products.[4]



On reduction (with hydriodic acid or zinc and hydrochloric acid) they are reduced to the corresponding chromanes (VI), while on distillation they lose one mole of water and form the corresponding chromenes (V), a behavior which is in accordance with similar phenomena observed on structurally related chromanols.[5]

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[3] Harries and Busse, *Ber.*, **28**, 502 (1895); **29**, 376 (1896); Zincke and Hohorst, *Ann.*, **353**, 377 (1907).

[4] Löwenbein, Pongrácz and Spiess, *Ber.*, **57**, 1517 (1924); Arndt and Pusch, *ibid.*, **58**, 1648 (1925).

[5] Heilbron and Hill, *J. Chem. Soc.*, **131**, 2005 (1927); Löwenbein and Rosenbaum, *Ann.*, **448**, 223 (1926).

The oxidation with chromic acid anhydride in glacial acetic acid yielded phenyl-substituted *iso*valeric acids (VII), the formation of which may also be regarded as a further support of the assigned formulas.

Experimental Part

For the preparation of practically all the condensation products to be described later the following process was used. To a molar mixture or solution of the monohydroxybenzene and mesityl oxide, one mole of concentrated sulfuric acid was added in small amounts. The temperature throughout the addition was kept at 0° to avoid objectionable tar formation. The mixture turned dark red. The flask containing the reaction mixture was then closed with a stopper having a calcium chloride drying tube attached, to prevent any absorption of moisture. To eliminate any further possibility of a violent after-reaction, the flask was kept in a water-bath the temperature of which was maintained at 15 to 20°.

On standing for a week the reaction mixture became solid, or at least semi-solid, indicating positive condensation. When no condensation took place (as in the case of ethers and esters), the material remained a mobile liquid, or in the same state as it had been originally.

Now cold water was added to the reaction mixture in excess, in order to extract the sulfuric acid and the phenylsulfonic acids that may have been formed in the reaction as by-products. After repeated washings of the reaction material with cold water, it was finally heated on a water-bath and treated with a large excess of hot water with constant stirring, in order to make the extraction of water-soluble products complete. At the temperature of the boiling water-bath the material usually melted. After cooling the water was decanted off. This operation was repeated until the wash water remained clear. At this stage the reaction product has the appearance of a dark, solid or semi-solid, gummy mass.

In the next step the solubility of the condensation product in 10% aqueous sodium hydroxide solution is tested. If it is soluble, the entire material is dissolved in hot 10% aqueous sodium hydroxide solution and filtered quickly while hot. The filtrate is then cooled to 0° or lower and ice-cold, dilute (5%) sulfuric acid added in small amounts. Since these condensation products are very sensitive toward acids (on account of the formation of colored decomposition products), any excess of the acid must be avoided and it is even favorable to keep the mixture just slightly alkaline. The condensation product (phenyl-substituted methyl *iso*butyl ketones or some chromanols) precipitates out and is filtered, or the supernatant liquid is decanted off and the residue repeatedly washed until free from inorganic substances. The product at this point should be light to golden yellow in color.

If the condensation product is insoluble in 10% aqueous sodium hydroxide solution (dichromanyl ethers), it is treated with a hot aqueous sodium or potassium hydroxide solution (10%) until the material acquires a yellow color. It is then cooled, whereby the product solidifies, and then well washed with hot and with cold water until free from alkalies. At this point, also, the product should have a bright yellow color.

The condensation products (the chromanols and the dichromanyl ethers) are insoluble in hot and cold water; some are soluble in dilute aqueous sodium hydroxide solution; they are soluble in alcohol, ether, chloroform, carbon tetrachloride, acetone, glacial acetic acid, benzene, petroleum ether, pyridine and concentrated sulfuric acid (deep red color). Since the products are quite difficult to crystallize, no general rule for their crystallization can be given, but it has been found that alcohol, ether, pyridine, benzene and ligroin are the most suitable crystallizing media.

In carrying out blank experiments under strictly similar reaction conditions with either mesityl oxide and sulfuric acid, or the monohydroxybenzenes and sulfuric acid, no such condensation products could be obtained.

TABLE I

COMPOUNDS PREPARED, MELTING POINTS AND ANALYTICAL DATA

	Mesityl oxide and	M. p., °C.	Analyses,[a] %		
Chromanol-2			Calcd.	Found	
2,2,4-Trimethyl-	Phenol	89	C, 75.00	75.15	75.20
$C_{12}H_{16}O_2$			H, 8.33	8.12	8.22
Dinitro derivative, $C_{12}H_{14}N_2O_6$		155	N, 9.92	9.74	9.78
7-Nitro-2,2,4-trimethyl-, $C_{12}H_{15}NO_4$	*m*-Nitrophenol	148	N, 5.91	5.88	5.95
6-Nitro-2,4,4-trimethyl-, $C_{12}H_{15}NO_4$	*p*-Nitrophenol	132	N, 5.91	5.87	5.89
2,4,4,8-Tetramethyl-	*o*-Cresol	120	C, 75.72	75.92	
$C_{13}H_{18}O_2$			H 8.73	8.50	
2,4,4,7-Tetramethyl-	Trinitro-*m*-cresol	120	C, 75.72	75.83	75.85
$C_{13}H_{18}O_2$			H, 8.73	8.90	8.88
Chromanyl ether-2					
Di-(2,4,4,7-tetramethyl)-	*m*-Cresol	58	C, 79.18	79.05	
$(C_{13}H_{19}O)_2O$			H, 8.54	8.32	
Tetranitro derivative $(C_{13}H_{15}N_2O_5)_2O$		145	N, 9.77	10.08	
Di-(2,4,4,6-tetramethyl)-	*p*-Cresol	57	C, 79.18	79.10	
$(C_{13}H_{17}O)_2O$			H, 8.54	8.22	
Tetranitro derivative $(C_{13}H_{15}N_2O_5)_2O$		167	N, 9.77	9.77	
Di-(5-chloro-2,4,4,7-tetramethyl)-	6-Chloro-*m*-cresol	71	C, 67.53	67.73	67.95
$(C_{13}H_{16}ClO)_2O$			H, 6.92	7.05	7.11
Di-(2,4,4,6,8-pentamethyl)-	1,3-Dimethyl-4-hydroxybenzene	Semi-solid			
$(C_{14}H_{19}O)_2O$			.....	...	
Tetranitro derivative $(C_{14}H_{17}N_2O_5)_2O$		155	N, 9.62	9.19	9.29
Di-(2,4,4.8-tetramethyl-*iso*propyl)-	Carvacrol	Semi-solid			
$(C_{16}H_{23}O)_2O$			.....	...	
Dinitro derivative $(C_{16}H_{22}NO_3)_2O$		185	N, 4.93	4.68	5.24
Di-(2,4,4,5-tetramethyl-8-*iso*propyl)-[b]	Thymol	136	C, 80.33	80.30	80.4
$(C_{16}H_{23}O)_2O$			H, 9.62	9.26	9.5
Dinitro derivative $(C_{16}H_{22}NO_3)_2O$		201	N, 4.93	5.05	5.15

[a] All of the quantitative determinations were carried out micro-analytically according to Pregl, "Quantitative Organic Micro-Analysis," P. Blakiston's Son and Co., Philadelphia, **1924**.

[b] Molecular weight: calcd., 478; found, 466, 505, 484.

Summary

1. New condensations of unsaturated ketones with phenols were investigated and the condensation system monohydroxybenzenes–mesityl oxide was studied. The condensation products are apparently chromanols or dichromanyl ethers, respectively.

2. These condensation products are valuable intermediates for the preparation of phenyl-substituted aldehydes and acids (by oxidation) and by the distillation of the acids or their sodium salts so obtainable, the corresponding *iso*propyl and *iso*butyl phenols can be synthesized; hence the condensation process just described furnishes an additional means for the introduction of alkyl groups into the benzene ring.

Further investigations of the condensation possibilities of unsaturated ketones, unsaturated aldehydes, unsaturated acids and unsaturated alcohols with phenols (both mono- and polyhydroxylic, mono- and polycyclic), aromatic hydroxy-aldehydes and aromatic hydroxy-acids are being carried on and positive results already have been obtained.

New York City

[Communication from the Laboratory of Organic Chemistry of the University of Wisconsin]

THE REACTIONS OF ALLYL ALCOHOL OVER ALUMINUM AND ZINC OXIDE CATALYSTS

By Paul E. Weston and Homer Adkins

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F. H. Constable[1] suggested that propionaldehyde was formed from allyl alcohol over *copper* through the intramolecular rearrangement of allyl alcohol, as in Equation 1.

$$CH_2{=}CHCH_2OH = CH_3CH_2CHO \qquad (1)$$

He demonstrated that it was not formed according to Equations 2 and 3

$$CH_2{=}CHCH_2OH = CH_2{=}CHCHO + H_2 \qquad (2)$$

$$CH_2{=}CHCHO + H_2 = CH_3CH_2CHO \qquad (3)$$

Evidence was presented in a previous paper[2] from this Laboratory that part if not all of the propionaldehyde formed over a *zinc oxide* catalyst from allyl alcohol resulted from the reduction of acrolein by allyl alcohol as in Equation 4

$$CH_2{=}CHCHO + CH_2{=}CHCH_2OH = CH_3CH_2CHO + CH_2{=}CHCHO \qquad (4)$$

It now seems certain that over alumina propionaldehyde is formed from allyl alcohol through intramolecular rearrangement. When allyl alcohol was passed over alumina at 330° gas was formed rapidly for a few minutes but the action died off within ten minutes after less than

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[1] Constable, *Proc. Roy. Soc. London*, **113A**, 254 (1926).

[2] Weston and Adkins, This Journal, **50**, 1930 (1928).