benzene to yield the red molecular compound VII, m.p. 156–157°, lit. m.p.: 156–157°[30,31a]; 158°.[8]

Anal. Calcd. for $C_{28}H_{18}O_3$: C, 83.56; H, 4.51; Mol. wt., 402. Found: C, 83.78; H, 4.71; Mol. wt., 202 (Rast camphor).[30,40]

A mixed m.p. of VI and VII was depressed to 130–145°. A benzene solution of VII was passed over aluminum oxide (Woelm, acid, activity grade 1). III fluoresces under ultraviolet light and the slow separation of VII into its components can be followed as III is eluted with large volumes of benzene. I remains adsorbed on the column.

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NEW YORK, N.Y.

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(40) Rast camphor, f.p., 159°; Mol. wts. of I and II are 194 and 208, respectively; average, 201.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, BUCKNELL UNIVERSITY]

Oxidation of Phenols by Periodate[1]

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Polyhydric phenols and their monomethyl ethers have been oxidized by periodic acid. The extent of the reaction is determined by the orientation of the hydroxyl groups in the ring. Those with vicinal hydroxyls consume three moles of periodate very quickly and a fourth mole more slowly. The extent and rate of oxidation is very nearly the same for all compounds studied. The phenols with meta oriented hydroxyls react more slowly; the extent of the reaction depends upon the number of hydroxyl groups in the molecule. Hydroquinone quickly consumes one mole of oxidant; methylation of one of the hydroxyl groups increases the extent of the reaction.

While there are many reports in the literature concerning the use of periodic acid and its salts as reagents for degrading 1,2-glycols and related substances, very little work has been done on the action of these oxidants on phenols. In 1935, Clutterbuck and Reuter[2] reported the successful oxidation of a 1,2-diketone containing the resorcinol structure but restricted their attention to changes in the aliphatic portion of the molecule. In 1946, Pennington and Ritter[3] published the preliminary results of an investigation of the action of periodic acid on certain phenols of interest in lignin research as well as on lignin sulfonic acids. They reported that the appearance of yellow to red colorations accompanied the oxidation of all phenols studied except resorcinol and phloroglucinol. Windrath[4] has utilized such colorations in the development of a color and precipitation test for polyhydric phenols.

Quite recently, three different investigators have attacked this problem in much greater detail. Adler[5] and his coworkers have carefully studied the action of sodium periodate on guaiacol and many compounds representing lignin models. Initial studies on simple molecules showed that compounds containing the guaiacyl structure liberated about 0.9 mole of methanol in the oxidation, and this was shown to be very general for this type of structure if oxidation took place. In addition, *cis-cis*-muconic acid was identified among the oxidation products of catechol itself. They have not, as yet, reported any findings on either oxidation with periodic acid or oxidations of resorcinol and hydroquinone structures. Stumpf and Rumpf[6] have also examined the action of sodium periodate on guaiacyl-containing structures as well as on catechol and resorcinol. They report that all three dihydric phenols consume periodate quickly. Ishikawa and Nakajima[7] have studied the action of periodic acid on lignin; their studies have included some work on phenols.

Another type of periodate oxidation involves the oxidation of an active hydrogen on a carbon between two carbonyl groups; the resulting substance can then be cleaved as in a normal periodate oxidation. There are numerous examples of this.[8–10] Recently, Wolfrom and Bobbitt[11] have shown that 1,3-cyclopentanedione and 1,3-cyclohexanedione

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(1) Presented before the Division of Organic Chemistry at the 132nd Meeting of the American Chemical Society, New York, September 1957.

(2) P. W. Clutterbuck and F. Reuter, *J. Chem. Soc.*, 1467 (1935).

(3) D. R. Pennington and D. E. Ritter, *J. Am. Chem. Soc.*, **68**, 1391 (1946); **69**, 187 (1947).

(4) O. M. Windrath, *Anal. Chem.*, **28**, 263 (1956).

(5) E. Adler and K. J. Bjorkvist, *Acta Chem. Scand.*, **5**, 241 (1951). E. Adler and S. Yllner, *Acta Chem. Scand.*, **7**, 570 (1953). E. Adler and S. Hernestam, *Acta Chem. Scand.*, **9**, 319 (1955).

(6) W. Stumpf and G. Rumpf, *Ann.*, **599**, 51 (1956).

(7) H. Ishikawa and T. Nakajima, *J. Japan Forest Soc.*, **36**, 106 (1954); **36**, 130 (1954). Trans. 62nd Meeting Japan Forest Soc., *J. Japan Forest Soc.*, Spec. Issue, 281 (1953). *Chem. Abstr.*, **50**, 3757h (1956).

(8) D. B. Sprinson and E. Chargaff, *J. Biol. Chem.*, **164**, 433 (1946).

(9) P. Fleury and J. Courtois, *Bull. soc. chim.*, [5] **14**, 358 (1947); [5] **15**, 190 (1948).

(10) C. F. Huebner, S. R. Ames, and E. C. Bubl, *J. Am. Chem. Soc.*, **68**, 1621 (1946).

(11) M. L. Wolfrom and J. M. Bobbitt, *J. Am. Chem. Soc.*, **78**, 2489 (1956).

TABLE I

PERIODIC ACID OXIDATION OF PHENOLS

Catechol (o-$C_6H_4(OH)_2$):								
Time (hr.)	2.5	21.5	45.5	69.5				
$\frac{\text{Moles } HIO_4 \text{ consumed}}{\text{Mole catechol}}$	2.98	3.78	3.95	4.03				
Guaiacol (o-$CH_3OC_6H_4OH$):								
Time (hr.)	3.0	22.0	45.5	68.5				
$\frac{\text{Moles } HIO_4 \text{ consumed}}{\text{Mole guaiacol}}$	3.21	3.90	4.04	4.16				
Pyrogallol (1,2,3-$C_6H_3(OH)_3$):								
Time (hr.)	0.5	5.0	23.5	54.5	126.5			
$\frac{\text{Moles } HIO_4 \text{ consumed}}{\text{Mole pyrogallol}}$	3.01	3.39	3.75	4.03	4.15			
Resorcinol (m-$C_6H_4(OH)_2$):								
Time (hr.)	1.0	5.2	23.5	51.4	92.4	144	186	264
$\frac{\text{Moles } HIO_4 \text{ consumed}}{\text{Mole resorcinol}}$	0.65	0.91	1.74	3.04	4.11	4.56	4.82	4.86
Resorcinol monomethyl ether (m-$CH_3OC_6H_4OH$):								
Time (hr.)	4.3	21.2	47	72	100	144	217	
$\frac{\text{Moles } HIO_4 \text{ consumed}}{\text{Mole of ether}}$	0.48	1.03	1.58	2.15	2.64	3.38	3.84	
Phloroglucinol (1,3,5-$C_6H_3(OH)_3$):								
Time (hr.)	1.2	4.2	9.4	29.5	51.8	94.3	169.5	312
$\frac{\text{Moles } HIO_4 \text{ consumed}}{\text{Mole of phloroglucinol}}$	2.18	3.03	4.14	5.78	6.13	6.50	6.60	6.87
Hydroquinone (p-$C_6H_4(OH)_2$):								
Time (hr.)	2.5	27.5	45.0					
$\frac{\text{Moles } HIO_4 \text{ consumed}}{\text{Mole of hydroquinone}}$	1.13	1.14	1.22					
Hydroquinone monomethyl ether (p-$CH_3OC_6H_4OH$):								
Time (hr.)	4.5	24.0	48.0	71.5	149.5			
$\frac{\text{Moles } HIO_4 \text{ consumed}}{\text{Mole of ether}}$	1.50	1.79	2.16	2.48	2.75			

consume periodate while noncyclic 1,3-diketones do not.

This paper reports the results of a study of the periodic acid oxidation of a number of phenols and their ethers. In most cases, deep colors developed which prevented a direct iodometric determination of the amount of periodate consumed. Even when the color was not pronounced fading end points were encountered when the reaction mixtures were titrated directly. Both these difficulties were overcome by use of the ion exchange procedure previously described.[12]

Results and Discussion. As has been reported by others[3,5,6] phenol and veratrole (1,2-dimethoxybenzene) were attacked only very slowly by periodic acid. For example, after periods of 2, 21, 45, and 69.5 hours, the amount of periodate consumed per mole of phenol was 0.18, 0.45, 0.72, and 0.92 mole respectively. After 65.5 hours, 0.45 mole of periodic acid per mole of veratrole was consumed. Data for the other compounds studied are summarized in Table I and plotted in Figures 1, 2, and 3.

The compounds listed in the first section of the table contain vicinal hydroxyl groups. These phenols all consumed about three moles of periodate rather quickly. The initial rapid consumption of three moles of oxidant was followed by a slower consumption of a fourth mole. The rate of oxidation was approximately the same for all three compounds as is indicated in Fig. 1. In all cases, the solutions eventually acquired a brownish color which rendered the solutions almost indistinguishable from one another.

The phenols with *meta* oriented hydroxyls studied are listed in the second section of the table. A quite different relationship exists among these phenols. Resorcinol slowly consumed somewhat more than four moles of oxidant. Its monomethyl ether was even more sluggish in its reaction. In the case of phloroglucinol, the reaction was more

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[12] M. A. Smith and B. R. Willeford, Jr., *Anal. Chem.*, 26, 751 (1954).

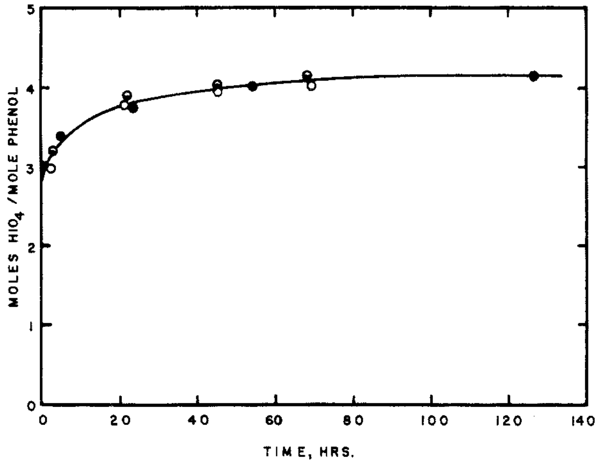


Fig. 1. Periodic acid oxidation of *ortho*-polyhydric phenols and derivatives. HIO_4 conc. = 0.01 M., *p*H = 2.1; open circles, catechol; half circles, guaiacol; closed circles, pyrogallol

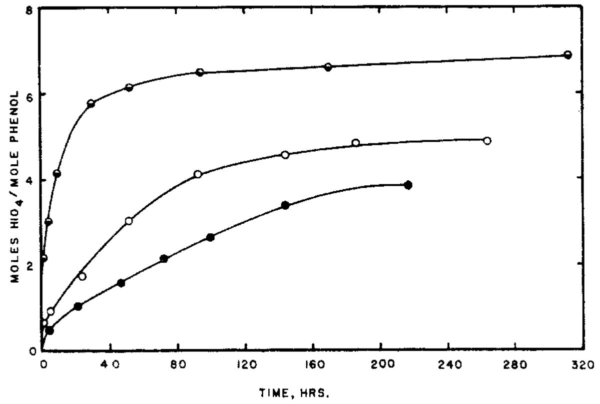


Fig. 2. Periodic acid oxidation of *meta*-polyhydric phenols and derivatives. HIO_4 conc. = 0.01 M., *p*H = 2.1; open circles, resorcinol; half circles, phloroglucinol; closed circles, resorcinol monomethyl ether

extensive and more rapid. About six moles of oxidant was quickly consumed, and this was followed by the slower consumption of a seventh mole. Fig. 2 summarizes these results.

The phenols with *para* oriented hydroxyl groups consumed less periodate than the members of the other two groups of polyhydric phenols. In the case of hydroquinone, only one mole of oxidant was consumed, and there was little further reaction. A light yellow color developed at once. Hydroquinone monomethyl ether was more reactive. It consumed over one mole of oxidant at once, and this was followed by a slower secondary reaction involving an additional one or two moles of periodate. These results are given in Fig. 3. The consumption of one mole of periodate by hydroquinone corresponds to the well known dehydrogenation of this compound.[13] Quinone was isolated in 89% yield from the reaction mixture.

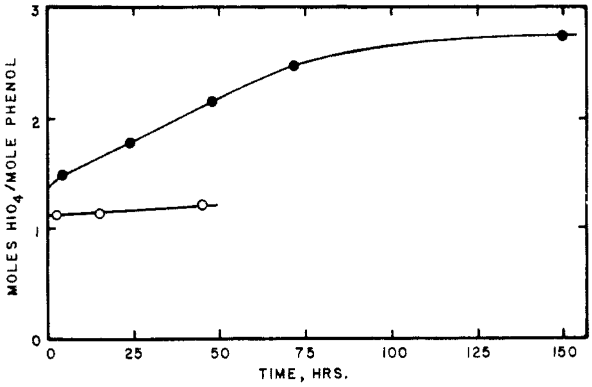
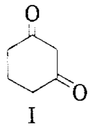


Fig. 3. Periodic acid oxidation of hydroquinone and its monomethyl ether. HIO_4 conc. = 0.01 M., *p*H = 2.1; open circles, hydroquinone; closed circles, hydroquinone monomethyl ether

That compounds such as phloroglucinol and resorcinol exhibit ketonic properties has been well established. Wolfrom and Bobbitt[11] found that 1,3-cyclohexandione(I) consumed four moles of periodate. One of their postulated intermediates is 2,3-dihydroxy-2-cyclohexenone(II); this was found to consume three moles of periodate. The keto forms of resorcinol (III) and pyrogallol (IV) differ from these compounds only in the presence of a double bond in the ring, and it is possible that the initial consumption of four and three moles of periodate by resorcinol and pyrogallol respectively proceeds by a similar process. That both the rate and extent of oxidation is very nearly the same for pyrogallol and catechol is quite remarkable, and that methylation of one of the hydroxy groups (guaiacol) has little effect is particularly striking. Further work to elucidate the mechanism of these oxidations is currently being carried out.



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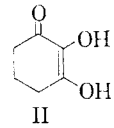

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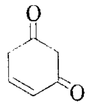
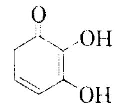


III



IV

EXPERIMENTAL

The experimental procedure was essentially the same as was reported previously.[12] Solutions of the phenol and periodic acid were prepared as described below for each compound studied. In all cases the *p*H of the solution was 2.1. At various intervals, 25 ml. aliquots (*ca.* 0.25 millimole of periodate) were withdrawn and passed through a 3 to 5 cm. bed of Amberlite IRA-400 ion exchange resin (acetate form) in an 8 mm. glass tube. A flow rate of 1 to 2 ml. per minute was used here and in the subsequent washing with 25 ml. of water. The column effluents were tested for iodate-periodate by the addition of an acidic potassium iodide–starch mixture. When the above procedure was followed, these tests were always negative. The periodate was then removed from the

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(13) R. Criegee in *Newer Methods of Preparative Organic Chemistry*, Interscience Publishers, Inc., New York, 1948, p. 18.

column with 150 ml. of 5% potassium hydroxide solution. This effluent was neutralized with sulfuric acid, buffered with solid sodium hydrogen carbonate, cooled and analyzed for periodate by the usual arsenite-iodine procedure.[14]

Catechol. Commercial catechol was recrystallized from toluene. The reaction mixture was 9.94×10^{-3} molar in periodic acid and 1.80×10^{-3} molar in catechol (initial ratio of reactants 5.52/1). A moderate orange color developed immediately, and did not change noticeably after the first few minutes.

Guaiacol. Redistilled, center cut, b.p. 205°. Periodic acid $9.92 \times 10^{-3}M$, guaiacol $1.99 \times 10^{-3}M$, reactant ratio 4.98/1. When the reactants were mixed a yellow color developed quickly. However, in less than three minutes the solution was indistinguishable from the catechol-periodate mixture described above.

Pyrogallol. Commercial C. P. grade, m.p. 131–133°. Periodic acid $9.92 \times 10^{-3}M$, pyrogallol $1.98 \times 10^{-3}M$, reactant ratio 4.99/1. A deep brown color developed quickly when the reactants were mixed. In time the color became less pronounced and approached that of the two mixtures described above.

Resorcinol. Recrystallized from benzene, m.p. 110°. Periodic acid $9.97 \times 10^{-3}M$, resorcinol $1.26 \times 10^{-3}M$, reactant ratio 7.89/1. There was no color change on mixing the reactants.

Resorcinol monomethyl ether. Redistilled, center cut, b.p. 128–128.5°/13. Periodic acid $9.90 \times 10^{-3}M$, compound $1.85 \times 10^{-3}M$, reactant ratio 5.35/1. A light yellow color slowly developed when the reactants were mixed.

Phloroglucinol. Recrystallized from hot water and dried to constant weight *in vacuo* at 65°. This process yields anhydrous phloroglucinol. Periodic acid $9.97 \times 10^{-3}M$, phloroglucinol $8.72 \times 10^{-4}M$, reactant ratio 11.4/1. No color change observed on mixing.

Hydroquinone. Recrystallized from water, m.p. 161°. Periodic acid $9.94 \times 10^{-3}M$, hydroquinone $2.06 \times 10^{-3}M$, reactant ratio 4.83/1. A light yellow color quickly developed upon mixing.

Hydroquinone monomethyl ether, m.p. 54°. Periodic acid $9.90 \times 10^{-3}M$, compound $1.88 \times 10^{-3}M$, reactant ratio 5.26/1. The reaction mixture was yellow after 24 hr., slowly changed to brown, and finally became cloudy.

Phenol. Redistilled center cut, b.p. 181°. Periodic acid $9.80 \times 10^{-3}M$, phenol $3.06 \times 10^{-3}M$, reactant ratio 3.20/1. The solution turned light yellow on mixing the reactants and after 24 hr. became cloudy.

Veratrole. Redistilled center cut, b.p. 205°. Periodic acid $9.92 \times 10^{-3}M$, veratrole $1.89 \times 10^{-3}M$, reactant ratio 5.25/1. Light yellow solution produced on mixing the reactants.

Acknowledgment. We wish to express our appreciation to the Research Corporation and to the E. I. du Pont de Nemours Co. for grants to the Bucknell University Chemistry Department which made this work possible. Some of the preliminary experiments were carried out by Mr. Donald Dietz.

LEWISBURG, PA.

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(14) E. L. Jackson, *Org. Reactions*, **2**, 341 (1944).

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Use of Nuclear Magnetic Resonance to Distinguish between Aliphatic Aldehyde and Ketone Derivatives

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The use of nuclear magnetic resonance to differentiate between aldehyde and ketone semicarbazones and 2,4-dinitrophenylhydrazones is described. The proton resonance of the N=C—H group of methylene chloride solutions of the dinitrophenylhydrazones occurs at −109 to −118 c.p.s. (at 40 Mc. relative to water as zero) and the corresponding resonance frequency of the semicarbazones is at −86 to −97 c.p.s. (40 Mc. relative to water) in the series of compounds studied. Other features of the NMR spectra are also discussed.

It has long been possible to distinguish aldehydes from ketones by standard chemical methods. In more recent years differences in physical properties, for example, differences in the carbonyl stretching frequency or the occurrence of the aldehydic C–H stretching band in infrared spectra, have been widely employed for the same purpose. However, in certain instances aldehydes and ketones, frequently liquids and obtained in low yield as degradation products, often from ozonolyses, can be isolated conveniently only as their derivatives. It is desirable, therefore, to have a method of determining whether such a derivative originated from an aldehyde or a ketone.

Ultraviolet[1–3] and infrared[2] spectral methods have been employed previously for this purpose. Thus, aldehyde 2,4-dinitrophenylhydrazones have been shown, in general, to have ultraviolet maxima at somewhat shorter wavelengths than those of similar derivatives of ketones,[1,2] while the color of the aldehyde derivatives deteriorated faster in basic solution than did that of the ketone derivatives.[2] In the infrared spectra of the dinitrophenylhydrazones of most compounds investigated the N–H stretching band was found at higher frequency in the ketone derivatives than in the aldehyde derivatives.[2] These correlations have proved useful; however, the shifts are slight and in marginal cases the ultraviolet and infrared spectral bands are

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(1) G. D. Johnson, *J. Am. Chem. Soc.*, **75**, 2720 (1953).

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(3) A. E. Gillam and E. S. Stern, *An Introduction to Electronic Absorption Spectroscopy in Organic Chemistry*, 2nd ed., Edward Arnold, Ltd., London, 1958, p. 60.