TABLE I

PHYSICAL PROPERTIES OF THE TETRAPHENYLETHANES

Compound	M.P.	Yield, %	Calcd. C	Calcd. H	Found C	Found H
1,1,1,2-Tetraphenylethane	143–144°	74 (78)[a]	See footnote[b]			
1,1,1-Triphenyl-2(*o*-tolyl)ethane	170–171°	65 (80)[a]	93.05	6.95	93.04	7.00
1,1,1-Triphenyl-2(*m*-tolyl)ethane	94–95°	70 (73)[a]	93.05	6.95	92.85	6.94
1,1,1-Triphenyl-2(*p*-tolyl)ethane	159–160°	78 (90)[a]	93.05	6.95	93.13	7.09

[a] The value in parenthesis is the yield obtained in the preparation of the authentic samples. [b] See C. B. Wooster and N. W. Mitchell, *J. Am. Chem. Soc.*, **52**, 688 (1930) where this compound is reported.

After the solution was stirred for 0.5 hr., an ethereal solution containing 5.6 g. (0.04 mole) of *o*-xylyl chloride[9] was added. The red color of the solution disappeared after the addition of the chloride was complete. The ammonia was evaporated, and 10 ml. of water was then added to the ether solution. The ether layer was separated, dried, and the solvent removed. The resulting white crystalline solid, (10.9 g.; 80%) after crystallization from a benzene–absolute ethanol solution melted at 170–171°. A mixed melting point and infrared spectrum showed this material was identical with that isolated from the reaction of *o*-xylene with triphenylmethyl.

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LAFAYETTE, IND.

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[9] M. Kharasch and H. C. Brown, *J. Am. Chem. Soc.*, **61**, 2142 (1939).

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE GEORGIA INSTITUTE OF TECHNOLOGY]

Methylene Derivatives as Intermediates in Polar Reactions. XXIV. The Reimer-Tiemann Reaction with Two *p*-Substituted Phenols[1]

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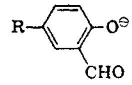
The Reimer-Tiemann reactions of *p*-cresol and *p*-hydroxybenzaldehyde have been studied. It is found that a *p*-methyl group increases and a *p*-formyl group decreases the rate of attack of dichloromethylene on the carbon atom *ortho* to the —O⁻ group. Attack at the *para* position of the *p*-cresolate anion is slower than at the *para* position of the phenoxide ion, perhaps because of steric factors.

In a previous paper evidence has been summarized that the Reimer-Tiemann reaction involves the combination of the phenoxide ion with a dichloromethylene molecule generated by the action of base on chloroform.[2] The relative rates of attack of dichloromethylene on the three centers of nucleophilicity of the phenoxide ion, namely the oxygen atom and the *ortho* and *para* carbon atoms, were also determined. In the present investigation we have studied two *p*-substituted phenols, *p*-hydroxybenzaldehyde and *p*-cresol, one with an electron-withdrawing substituent and the other with an electron-donating substituent.

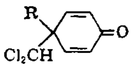
RESULTS AND DISCUSSION

If it is assumed that, in the relatively dilute solutions with which we have worked, the attack of dichloromethylene on the *ortho* and *para* carbons and the oxygen atom of the *p*-cresolate anion leads inevitably to the 2-formyl-4-methylphenoxide ion, 4-dichloromethyl-4-methylcyclohexa-2,5-dienone and unchanged *p*-cresolate anion, respectively, the reaction paths open to dichloromethylene may be written:

$$CCl_2 + p\text{-}RC_6H_4O^- \xrightarrow{k_o}$$



$$CCl_2 + p\text{-}RC_6H_4O^- \xrightarrow{k_p}$$



$$CCl_2 + p\text{-}RC_6H_4O^- \xrightarrow{k_{ox}} p\text{-}RC_6H_4O^- + CO \text{ or } HCO_2^-$$

$$CCl_2 + H_2O \xrightarrow{k_w} CO \text{ or } HCO_2^-$$

$$CCl_2 + OH^- \xrightarrow{k_h} CO \text{ or } HCO_2^-$$

where R = CH_3. A derivation like that used previously[2] shows

$$\frac{1}{f_o} = 1 + \frac{(k_p/k_w) + (k_{ox}/k_w)}{(k_o/k_w)} + (k_w/k_o)\frac{[H_2O] + (k_h/k_w)[OH^-]}{[RC_6H_4O^-]} \quad (1)$$

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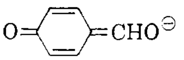
[1] For part XXIII in this series see J. Hine and J. J. Porter, *J. Am. Chem. Soc.*, **82**, 6178 (1960).

[2] J. Hine and J. M. van der Veen, *J. Am. Chem. Soc.*, **81**, 6446 (1959). For a recent review on the Reimer-Tiemann reaction see H. Wynberg, *Chem. Revs.*, **60**, 169 (1960).

where f_o is the fraction of the chloroform that reacts that gives the *ortho* substitution product. When the data obtained in aqueous solution at 35° was plotted, using Equation 1 as previously,[2] it gave a fair approach to a straight line whose slope showed k_o/k_w to be 70. While the slope was found to be reproducible, the intercept was not. Thus the value 15 for k_{ox}/k_w that we have calculated from the intercept may be quite unreliable. For k_p/k_w a value of 17 was calculated from the fact that 24 ± 7% as much *para* as *ortho* substitution was noted.

The case of *p*-hydroxybenzaldehyde is slightly different from that of *p*-cresol in that there seems to be another plausible point at which dichloromethylene might attack its anion. This, of course, is the aldehydic oxygen atom, which may bear a considerable negative charge due to the contribution of structures such as



As any intermediate thus formed would be expected to be hydrolyzed to the *p*-hydroxybenzaldehyde, we shall redefine k_{ox} in the present case so as to govern reaction at both of the oxygen atoms of the conjugate base of *p*-hydroxybenzaldehyde. The value of k_o/k_w obtained for this compound from the slope of a plot of Equation 1 was 20. While we have not isolated the product of *para* attack, which does not appear to be a known compound, from the intercept of the plot for the *ortho* product a value of 60 may be calculated for $(k_p/k_w) + (k_{ox}/k_w)$.

The k_o/k_w values of 70, 46.5, and 20 obtained for the anions of *p*-cresol, phenol,[2] and *p*-hydroxybenzaldehyde, respectively, are in the order expected since the electron-donating methyl group was expected to increase the nucleophilicity and the electron-withdrawing formyl group to decrease the nucleophilicity of the ortho carbon atom of the phenoxide ion. The decreased value of k_p/k_w for *p*-cresol may reasonably be attributed to a steric effect, while the k_{ox}/k_w values are too uncertain in magnitude and significance to permit interpretation.

In order to learn the importance of temperature on orientation in the Reimer-Tiemann reaction we determined values of k_o/k_p for the phenoxide ion, by the method described previously.[2] In the presence of 1.08*M* sodium phenoxide and 0.83*M* sodium hydroxide, values of 0.93, 1.00, and 1.02 were obtained at 20°, 50°, and 60°, respectively.

EXPERIMENTAL

Reagents. Technical *p*-hydroxybenzaldehyde was recrystallized to give pale yellow needles, m.p. 115.9–116.0° (reported[3] m.p. 115–116°); *p*-cresol (Matheson-redistilled) was fractionally distilled under nitrogen and material of b.p. 201.5–202.5° used; 4-dichloromethyl-4-methylcyclohexa-2,5-dienone, m.p. 54–55° (reported[4] m.p. 55°), and 2-hydroxy-5-methylbenzaldehyde, m.p. 55–56° (reported[5] m.p. 56°), were prepared from *p*-cresol, chloroform, and alkali[4,5]; 2,4-diformylphenol, m.p. 106–107° (reported[6] m.p. 108°), was prepared analogously from salicylaldehyde.[6]

Measurement of f_0 and f_p. For *p*-hydroxybenzaldehyde, values of f_0 were determined by a method like that used previously for phenol.[2] The ultraviolet measurements were made on basic solutions at 3900 Å where the product, 2,4-diformylphenol, absorbs strongly (ϵ 3073) and the reactant almost negligibly (ϵ 2.8). In the study of *p*-cresol, measurements were also made at 3900 Å. to determine the concentration of 2-hydroxy-5-methylbenzaldehyde (ϵ 6050) and neither the reactant nor the *para* substitution product absorbed detectably. Following this measurement, the alkaline *p*-cresol reaction mixtures were extracted with cyclohexane to remove the 4-dichloromethyl-4-methylcyclohexa-2,5-dienone whose concentration was then determined by measurements at 2270 Å (ϵ 13540), after the cyclohexane solution had been washed with aqueous alkali. The results obtained in one run on *p*-hydroxybenzaldehyde are listed in Table I.

TABLE I

YIELDS OF 2,4-DIFORMYLPHENOL FROM *p*-HYDROXYBENZALDEHYDE, CHLOROFORM, AND SODIUM HYDROXIDE IN AQUEOUS SOLUTION AT 35° [a]

$[\mathrm{NaC_7H_5O_2}]_0$	$[\mathrm{NaOH}]_0$	f_0[b]
0.336	0.364	0.069
.245	.390	.061
.226	.353	.046
.161	.348	.039
.144	.363	.037
.124	.383	.033
.117	.363	.032
.089	.341	.024

[a] $[\mathrm{CHCl_3}]_0$ ~0.026 in all cases. [b] Yield of 2,4-diformylphenol based on chloroform that reacted.

Our data in the present cases seemed in general to be less reproducible than those obtained in the study of phenol.[2] This may have resulted from the partial destruction of some of the products, particularly the cyclohexadienone, under the reaction conditions. It might also be mentioned that errors in the value we have used for k_h/k_w lend particular uncertainty to the values of $k_{ox}/k_w + k_p/k_w$ obtained with *p*-hydroxybenzaldehyde whose conjugate base is rather weakly nucleophilic.

Acknowledgment. We should like to acknowledge our indebtedness to the Alfred P. Sloan Foundation for aid in the support of this investigation.

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(3) K. Reimer and F. Tiemann, *Ber.*, **9**, 824 (1876).

(4) K. Auwers, *Ann.*, **352**, 219 (1907).

(5) F. Tiemann and C. Schotten, *Ber.*, **11**, 767 (1878).

(6) H. Voswinckel, *Ber.*, **15**, 2021 (1882).