O.D. readings at 645 mμ were followed in studying the rates of converstion of the *b* series of compounds. This wave length was selected because it was found to be the red-peak in the difference-spectra of chlorophyll *b* and pheophytin *b*. This finding has since been confirmed by Vernon.[10]

Trial runs were made with different buffer systems and aqueous hydrochloric acid solutions. All the buffer systems tried turned turbid when added to acetone solutions of the pigments to initiate the reaction. The aqueous hydrochloric acid solutions did not exhibit this difficulty and were therefore used in these studies. Acid was added to give a H^+ concentration of 1×10^{-4} in the 80% acetone reaction mixture. At this acid concentration the reaction rate was neither too fast at the elevated temperature nor too slow at the lower temperatures. The reduction in volume due to the hydration of the acetone molecules was taken into consideration in preparing this mixture. Hydrogen ions were in 10–100-fold excess of pigment concentration under the conditions used.

The concentration of pigment in the reaction mixture was adjusted to give an initial O.D. reading of about 0.43 in order to be within the range of greatest accuracy of the instrument and a range of concentration in which Beers law is followed, as indicated by series of tests. Preliminary trials where ΔOD was plotted *vs.* *t* for different chlorophyll concentrations indicated that the reaction was first order with respect to chlorophyll concentration.

Fifteen to twenty O.D. readings were taken during the course of each test, each of which was made in triplicate, to reduce the errors owing to instrumental inconsistencies on the rate factors. The conversion reaction was followed to at least 75% completion, following which it was completed by addition of a small crystal (8–10 mg.) of oxalic acid to the reaction vessel. The reaction was then assumed to be complete when the O.D. reacted a constant value.

(10) L. P. Vernon, *Anal. Chem.*, **32**, 1144 (1960).

The Baeyer–Villiger Condensation. I. *ortho*-Tritylation of Phenols

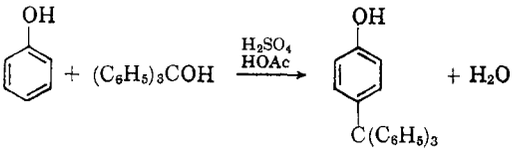
ALEXANDER T. SHULGIN

The Dow Chemical Company, Western Division, Pittsburg, California

Received February 19, 1962

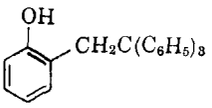
Procedures have been developed which permit the introduction of a trityl group *either ortho* or *para* to a phenolic hydroxyl group, within the limitation of steric influences of other substituents present. The generality of these specific procedures has been explored.

The introduction of the triphenylmethyl (trityl) group into the aromatic ring to form a triphenylarylmethane has often been referred to as the Baeyer-Villiger condensation, in recognition of the first observation and study of the reaction in 1902.[1] The initial observations were of the reaction between triphenylcarbinol and phenol in acetic acid, under the influence of sulfuric acid, to produce *para*-tritylphenol. Since that time, the reaction has been extended and found to embrace a large number of variations.



The triphenylcarbinol portion of the equation may be replaced with any equivalent that is capable of forming a stable carbonium ion, such as triphenylmethyl chloride[2] or the dichlorophosphonyl ether, $(C_6H_5)_3COPCl_2$.[3] In addition to alkylphenols, the reaction occurs with halophenols,[4] phenyl ethers,[1,3] anilines,[3c,4] and even unactivated alkyl-substituted benzenes.[5] Catalysts employed include sulfuric acid, hydrochloric acid,[5] perchloric acid,[6] zinc chloride[2a,7] or by direct fusion of the components without the intervention of any catalyst at all.[2a,2b,4] The presence of negative groups on a phenol, such as a nitro[3] or carbonyl,[8] prevents the reaction from occurring.

The structure of the tritylation products has been the subject of several investigations. Initial assignments as O-trityl ethers (to account for the lack of phenolic properties of the products) were disproven by the preparation of a true trityl phenyl ether by the direct action of triphenylmethyl chloride upon potassium phenolate.[2a] Aliphatic tritylation, exemplified by the suggested structure for the tritylation



product of *o*-cresol,[9] has been disproven both by the independent synthesis of the above ethane compound by a different route[10] (which proved to be a different material), as well as by the independent synthesis of *p*-trityl-*o*-cresol[11] (which proved to be identical with the *o*-cresol tritylation product).

(1) A. Baeyer and V. Villiger, *Ber.* **35**, 3013 (1902).

(2)(a) A. Baeyer, *Ber.* **42**, 2624 (1909). (b) M. Busch and R. Knoll, *Ber.*, **60**, 2243 (1927). (c) P. Schorigin, *Ber.*, **60**, 2373 (1927).

(3)(a) D. R. Boyd and G. Chignell, *J. Chem. Soc.*, 813 (1923). (b) D. R. Boyd and F. J. Smith, *ibid.*, 1477 (1924). (c) D. R. Boyd and D. V. N. Hardy, *ibid.*, 630 (1928).

(4) D. V. N. Hardy, *ibid.*, 1000 (1929).

(5) C. A. MacKenzie and G. Chuchani, *J. Org. Chem.*, **20**, 336 (1955).

(6) H. Burton and G. W. H. Cheeseman, *J. Chem. Soc.*, 832 (1953).

(7) J. van Alphen, *Rec. Trav. Chim.*, **46**, 288 (1927).

(8) N. P. Buu-Hoï, *J. Org. Chem.*, **22**, 666 (1957).

(9) P. Schorigin, *Ber.*, **59**, 2502 (1926).

(10) H. A. Iddles, K. S. French, and E. F. Mellon, *J. Am. Chem. Soc.*, **61**, 3192 (1939).

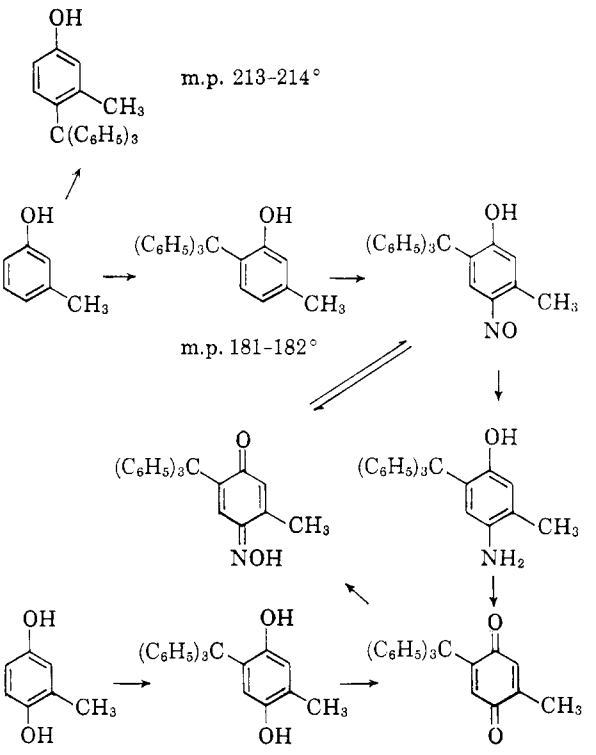
(11) H. A. Iddles and H. L. Minckler, *ibid.*, **62**, 2757 (1940).

The positional assignment of the trityl group has been less rigidly established. That the substitution of the trityl group had occurred in the *para* position, in the tritylation of *o*-cresol, had been, as mentioned above, established by independent synthesis. With *m*-cresol, however, the product had been assumed, initially and without supporting evidence, to be an *o*-trityl compound.[9] The product, whether prepared by the usual Baeyer–Villiger procedure,[2c] or employing either triphenylmethyl chloride[9] or the phosphonyl chloride,[3c,12] is the *para* isomer as established by the unambigious synthesis of the true *ortho* isomer, described below.

Except for a single report of successful tritylation of 4-bromo-2-cresol,[13] there are no instances of the introduction of a trityl group *ortho* to a directing substituent in an aromatic ring. In polyfunctional aromatics, *ortho* tritylation has been quite well established (resorcinol yields 4-tritylresorcinol;[4,14] 1,4-dihydroxynaphthalene and 2,7-dihydroxynaphthalene yield 2-trityl and 7,*x*-dityrityl products respectively).[8] However, in the phenolic system, the rule of thumb has been expressed: if tritylation cannot occur *para* to a directing group, it will not occur at all.[4,8]

Although the classic conditions of the Baeyer–Villiger reaction lead, in every reported case, to *para* tritylation, it has been found here that, with elevated temperature, restriction of acid catalyst, exclusion of acetic acid, and employment of excess phenol as solvent, tritylation will occur, in those instances where steric geometry is encouraging, *ortho* to the directing group.

With *m*-cresol, although the 4-trityl-3-cresol isomer (m.p. 213–214°) is produced as described in the several references above, conditions as described in the experimental section lead to the *ortho* isomer exclusively (m.p. 181–182°). The establishment of this orientation is obvious from the following flowsheet.



The *p*-nitrosophenol, obtained from the low melting isomer of trityl-*m*-cresol, is identical (m.p., m.m.p., and infrared scan) to the "monooxime" of 2-methyl-5-trityl-benzoquinone obtained from the quinone that is obtained upon oxidation of the tritylation product of tolylhydroquinone.[15] Although this positional assignment has been established by direct synthetic proof, most of the similar assignments discussed in this article are based upon the spectroscopic analysis of the "intramolecularly-bonded" —OH group, a technique expanded upon in the following paper of this series.[16] It has been observed that in the *para* tritylated *m*-cresol isomer, the phenolic hydroxy group is, as with phenol, completely unbonded when dissolved in carbon tetrachloride at a concentration ($5 \times 10^{-3} M$) that precludes intermolecular hydrogen bonding. In all instances of *ortho* tritylation, the availability of a hydrogen-bonding base produces a *cis-trans* bonding isomerization recently explored[16] in more detail.

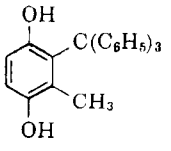
The two extreme sets of conditions that lead to specific positional substitution, may be designated Procedure A, *para* tritylation, realized with gross amounts of sulfuric acid as catalyst and acetic acid at room temperature; and Procedure B, leading to *ortho* tritylation, employing excess phenol as solvent and only a catalytic amount of sulfuric acid, at steam bath temperatures.[17] In addition, steric conditions must be at hand that specifically

(12) H. H. Hatt, *J. Chem. Soc.*, 776 (1933).

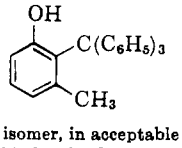
(13) H. A. Iddles, W. H. Miller, and W. H. Powers, *J. Am. Chem. Soc.*, **62**, 71 (1940).

(14) R. Meyer and O. Fischer, *J. Paak. Chem.*, **82**, 521 (1910).

(15) It is recognized that the unlikely vicinal tritylation product of tolylhydroquinone cannot rigidly be excluded in this reasoning, and that,



therefore, the *ortho*-triytlation product of *o*-cresol could conceivably be



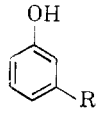
The formation of a single isomer, in acceptable yields, in both reaction, speaks against this more hindered substitution.

(16) See "The Baeyer–Villiger Reaction, II," *Spectrochim. Acta*, in press.

(17) Attempted interchanging of the conditions was not advantageous. *m*-Cresol and triphenylcarbinol, with a catalytic amount of sulfuric acid at room temperature, led to a nearly equal mixture of the two isomers, whereas an acetic acid solution of the reactants containing gross amounts of sulfuric acid, at 100°, led to extensive tarring. The latter condition, with the more hindering *m*-substituent, leads to *o*-tritylation.

encourage the achieved orientation of the trityl group. With all *ortho*-alkyl phenols yet observed, only *para* tritylation has been achieved, regardless of which procedure is employed. *o*-Cresol, *o*-*tert*-butylphenol, *o*-phenylphenol, and *o*-cyclohexylphenol all lead exclusively to a *para*-trityl product. The variously substituted *meta*-alkyl phenols, however, provided excellent illustrations of the effectiveness of the two routes of tritylation. Table I itemizes the results of the two tritylation procedures on various *meta* substituted phenols which embody extremes of steric hinderance.

TABLE I
ORIENTATION OF TRITYLATION



R	Result with procedure A	Result with procedure B
—H	*para*	*para*
—CH_3	*para*	*ortho*
—CH_2CH_3	*ortho*[a]	*ortho*
—$CH(CH_3)_2$	*ortho*	[b]
—$C(CH_3)_3$	*ortho*	*ortho*

[a] The ditrityl derivative was the major product.
[b] Triphenylmethane was isolated as the sole product.

As is readily apparent, as the steric blockage of the *para* position increases, the ease of *ortho*-substitution increases to the extreme realized in *m*-*tert*-butylphenol, wherein only the *ortho*-trityl isomer may be obtained under either set of conditions.

With a *para* substituted phenol, there has heretofore been no satisfactory description of tritylation. In attempted reactions with *p*-cresol, the normal Baeyer–Villiger conditions employing triphenylcarbinol are reported to yield exclusively triphenylmethane,[4] whereas both triphenylmethyl chloride[2c] and triphenoxyphosphenyl dichloride[3c] lead to products of unestablished structure. A single attempt to tritylate *p*-*tert*-amylphenol was reported unsuccessful.[8] It has been found that *p*-*tert*-butylphenol tritylates quite smoothly (although slowly) via procedure A to 2-trityl-4-*tert*-butylphenol.

Yet another instance of the prediction of extremes in positional assignment is found in 3,5-xylenol. This phenol may be substituted either between the methyl groups (*para*-tritylation *via* Procedure A) or *ortho*- to the phenolic hydroxyl group (Procedure B). Attempts to reproduce the reported *para*-tritylation of 2,3,5-trimethylphenol[8] have been unsuccessful, although the assignment of 4-substitution of the trityl group in thymol is confirmed. An attempt to introduce this group *ortho* to the phenolic hydroxy group was unsuccessful. The extent of the applicability of the above procedures is being pursued as well as the chemistry of the tritylation of polyfunctional aromatic systems.

Experimental[18]

Procedure A (*para*-**Tritylation**).—To 10 g. of the phenol in 100 ml. of acetic acid, there was added 10 g. of triphenylcarbinol, the mixture being heated, if necessary, to effect solution. The cooled solution was then treated with 16 g. of concd. sulfuric acid. After spontaneous crystallization had set in (several weeks may be required) the product was removed by filtration and washed thoroughly with acetic acid before recrystallization.

Procedure B (*ortho*-**Tritylation**).—In 20 g. of the melted phenol, there was dissolved 10 g. of triphenylcarbinol. The solution was brought to 100° on the steam bath, then treated with few drops of concd. sulfuric acid. It was held at 100° until the intense color had faded and the production of solid products was extensive (2 days was usually sufficient). In some instances specified, a shorter period was essential. The product was triturated under a small amount of methanol, filtered, washed sparingly with methanol, and recrystallized.

Acetylations were achieved by allowing the phenol to reflux in an excess of acetic anhydride and sodium acetate, followed by digestion in water, removal of the ester by filtration, and crystallization from an appropriate solvent, as noted in Table II.

Brominations were conducted in acetic acid, with a slight excess of bromine, and held at steam bath temperature until color was discharged. The product was recrystallized as noted.

The results of the application of these procedures to a variety of substituted phenols are compiled in Table II.

4-Nitroso-$\alpha^2,\alpha^2,\alpha^2$-triphenyl-2,5-xylenol; 5-Methyl-4-nitroso-2-tritylphenol. From 2-Trityl-5-cresol.—A solution of 1.40 g. of 2-trityl-5-cresol in 25 ml. of absolute ethanol was cooled to 0° and diluted, with vigorous stirring, with 4 ml. of conc. hydrochloric acid. To the suspension of finely divided phenol was added 0.50 g. of powdered sodium nitrite. The suspension was stirred as it slowly returned to room temperature and the stirring continued for 17 hr. The pale yellow product (a mixture of starting phenol and the desired *p*-nitroso derivative) was filtered and washed thoroughly with water. After drying, this crude product was suspended in 50 ml. of warm toluene (the starting phenol dissolved readily) and the insoluble nitroso product was removed by filtration. Washing with additional toluene and air-drying yielded 0.30 g. of bright yellow solid, m.p. 243° with decomposition. Conversion was 20% with a yield of 92% based upon recovered starting material.

Purification of the product may be achieved by extraction with aqueous ammonia, but this more cumbersome separation does not improve the purity or the yield.

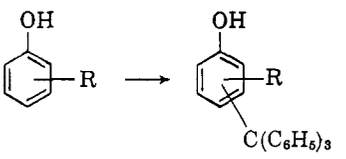
Anal. Calcd. for $C_{26}H_{21}NO_2$: C, 82.30; H, 5.58; N, 3.69. Found: C, 82.53; H, 5.54; N, 3.54.

From 2-Trityl-5-methylquinone.—To a solution of 3.6 g. of 2-trityl-5-methylquinone (see preparation below) in 140 ml. of boiling anhydrous alcohol was added, in sequence, a solution of 1.4 g. of hydroxylamine hydrochloride in 8 ml. of water and a solution of 0.8 g. of anhydrous sodium acetate in 8 ml. of water. The solution was refluxed for 0.5 hr. during which time the color became deep red. After cooling to room temperature, the solution was diluted fourfold with water and the solid so precipitated, filtered, washed with water, and finally with hot toluene. Thus, there was obtained 2.6 g. (70% yield) of a bright yellow solid, identical to the nitrosophenol described above.

4-Amino-$\alpha^2,\alpha^2,\alpha^2$-triphenyl-2,5-xylenol; 4-Amino-5-methyl-2-tritylphenol.—To a solution of 2.5 g. of the above nitroso

(18) All melting points reported below are uncorrected. Except where verified by alternate synthesis, the structural assignments depend upon analysis and spectroscopic integrity (see ref. 16).

TABLE II



R	Procedure	Time		Position $C(C_6H_5)_3$	M.p.[a] derivatives	
H	A	3	D	4	285–285.5° (90%) Et[b]	Acetate, 174–175° (96%) Cy[c]
	B	1	H	4	284–285° (46%) Et	
2-CH_3	B	5	H	4	182–183° (79%) Et[d]	
2-$C(CH_3)_3$	A	3	D	4	173–174° (60%) Me[e]	Acetate, 124–126° (96%) He[f] 6-Bromo, 148–149° (95%) Ac[g]
	B	0.5	H[h]	4	173–174° (78%) Me	
2-C6H5	A	12	H	4	234–236° (50%) Ac[i]	Acetate, 209–210° (76%)[j] 6-Bromo, 155° (83%) Ac[k]
	B	0.5	H	4	236–238° (56%) Ac	
2-C6H11	A	1	H	4	191–192° (57%) Cy[l]	Acetate, 126–127° (92%) Et[m] 6-Bromo,[n] 204–205° (85%) Bz[o]
	B	0.7	H	4	191–192° (77%)	
3-CH_3	A	1	D	4	213–214° (45%) Me[p]	Acetate, 199–200° (85%) Et[q] 2,6-Dibromo, 176–177° (81%) Mw[r]
	B	1	D	6	181–182° (25%) Me[s]	Acetate, 174–176° (85%) Et[t] 2,4-Dibromo, 172–173 (85%) Ac[u]
3-CH_2CH_3	A	9	D	6[v]	154–155° (7%) Et[w]	
	B	3	D	6	154–155° (52%) Et	
3-$CH(CH_3)_2$	A	9	D	6[x]	192–193° (23%) Et[y]	
	B	3	D	..	(0%)	
3-$C(CH_3)_3$	A	20	D	6	200–201° (68%) Cy[z]	Acetate, 172–173 (87%) Et[aa]
4-CH_3	B	4	D	[bb]		
4-$C(CH_3)_3$	A	60	D	2	147–148° (20%) Mw[cc]	Acetate, 145–146° (70%) Et[dd]

[a] All melting points uncorrected. Also included are yield and recrystallization solvent—*i.e.*, Ac = acetic acid, Cy = cyclohexane, Me = methanol, Et = 95% ethanol, He = hexane, Bz = benzene, Mw = methanol, and water. [b] Lit. 282° (see ref. 1). [c] Lit. 175° [see A. Bistrzycki and J. Gyr, *Ber.*, **37** 655 (1904)]. [d] Lit., 182–183° (see ref. 10). [e] Contains four molecules of MeOH of crystallization. Calcd. for $C_{33}H_{44}O_5$: C, 76.11; H 8.52. Found: C, 76.23; H 8.51. [f] Calculated for $C_{31}H_{30}O_2$: C 85.67; H 6.96. Found C 85.48; H 6.85. [g] Calculated for $C_{29}H_{27}BrO$: C 73.88; H 5.77. Found C 73.38; H 5.16. [h] If the reaction is allowed to proceed until the color is discharged (4 days), *p*-tritylphenol (by acid-catalysed debutylation) is obtained in 78% yield. [i] Lit. 246–247° (see ref. 9). [j] The product was purified by extraction with boiling hexane. Calcd. for $C_{33}H_{26}O_2$: C 87.19; H 5.77. Found: C 87.42; H 5.81. [k] A molecule of acetic acid of crystallization could not be satisfactorily removed. Calculated for $C_{33}H_{27}BrO_3$: C 71.86; H 4.93; equil. wt. 275.5. Found: C 72.08; H 5.04; equil. wt. 275.5 (KOH in acetone; both breaks were distinct). [l] Calcd. for $C_{31}H_{30}O$: C 88.95; H 7.22. Found: C 88.95; H 7.04. [m] Calcd. for $C_{33}H_{32}O_2$: C 86.05; H 7.00. Found: C 86.20; H 7.13. [n] Prepared in $CHCl_3$. [o] Solvent removed only after prolonged drying at 56°. Calcd. for $C_{31}H_{29}BrO$: C 74.84; H 5.87. Found: C 74.91; H 6.06. [p] Lit. 213–214° (see ref. 3c). [q] Calcd. for $C_{28}H_{24}O_2$: C 85.68; H 6.16. Found C 84.92; H 6.13. [r] Calcd. for $C_{26}H_{28}BrO\cdot H_2O$: C 59.34; H 4.21. Found: C 59.63; H 4.20. [s] Calcd. for $C_{26}H_{22}O$: C 89.11; H 6.33; equiv. wt. 350. Found: C 89.03; H 6.38; equiv. wt. (Br^-, BrO_3^-) 357. [t] Calcd. for $C_{28}H_{24}O_2$: C 85.68; H 6.16. Found: C 85.29; H 6.31. [u] Calcd. for $C_{26}H_{20}Br_2O\cdot CH_3COOH$: C 59.17; H 4.26; Br 28.12; equiv. wt. 284. Found: C 59.58; H 4.25; Br 27.54; equiv. wt. 282 (KOH in acetone; both breaks were distinct). [v] The ditrityl derivative was the principal product. See Experimental. [w] Calcd. for $C_{27}H_{24}O$: C 88.97; H 6.64. Found: C 89.12; H 6.71. [x] As with the ethyl isomer, a methanol-insoluble side product was isolated (presumably a ditrityl isomer), m.p. 294–298° from tetrahydrofuran–methanol. [y] Calcd. for $C_{28}H_{26}O$: C 88.85; H 6.92. Found: C 89.02; H 6.81. [z] Calcd. for $C_{29}H_{28}O$: C 88.73; H 7.19. Found: C 88.61; H 7.30. [aa] Calcd. for $C_{31}H_{30}O_2$: C 85.68, H 6.96. Found C 85.48; H 7.33. [bb] Spectrophotometric analysis showed very small, but distinct absorption at ~3545 $cm.^{-1}$, implying *ortho* tritylation. No product was isolatable. [cc] Calcd. for $C_{29}H_{28}O$: C 88.73; H 7.19. Found: C 88.70; H 7.32. [dd] Calcd. for $C_{31}H_{30}O_2$: C 85.68; H 6.96. Found: C 85.83; H 6.80.

phenol in 25 ml. of hot acetic acid, there was added zinc dust in small portions until the initial darkening had lightened and no further evidence of color loss was obtained with addition of more zinc. The nearly colorless solution was filtered free of the unchanged zinc, which was washed with small volumes of hot acetic acid. The combined filtrates were flooded with water and the acetic acid neutralized with base. The precipitated solid was triturated under a small amount of methanol, then recrystallized from 95% ethanol, yielding 1.7 g. of a white crystalline solid that turned mauve on standing. The m.p., 196.5–199°, was not improved on recrystallization.

Anal. Calcd. for $C_{26}H_{23}NO$: C, 85.45; H, 6.34; N, 3.83; equiv. wt. 365. Found: C, 85.21; H, 6.41; N, 3.60; eq. wt. 360 ($HClO_4$).

α,α,α-Triphenyl-2,5-dimethylhydroquinone; 5-Trityl-2-p-tolylhydroquinone.—A mixture of 8 g. of triphenylcarbinol and 8 g. of *p*-tolylhydroquinone in 50 ml. of glacial acetic acid was heated on the stream bath until complete solution was effected. The darkened solution was quickly cooled to 35° (there should not be any crystallization of the carbinol) and treated with 6 ml. of concentrated sulfuric acid. There was immediate darkening accompanied by an exothermic reaction. After standing at room temperature for 24 hrs., the thick black mass was filtered with suction, and the resulting crystals washed with small amounts of acetic acid.

The straw-colored product, upon crystallization from toluene yielded clusters of white needles weighing 5.2 g. and had a m.p. of 213.5–215.5°.[19]

Anal. Calcd. for $C_{26}H_{22}O_2$: C, 85.22; H, 6.05. Found: C, 85.37; H, 5.98.

The diacetate, from treatment with an excess of acetic anhydride and sodium acetate, was obtained in a 71% yield after recrystallization from methanol (60 ml./g.); white granular crystals, m.p. 159–160° (with prior sintering at 149°).

Anal. Calcd. for $C_{30}H_{26}O_4$: C, 79.98; H, 5.82. Found: C, 79.96; H, 5.98.

α,α,α-Triphenyl-2,5-xylylquinone; 2-Methyl-5-trityl-benzoquinone. From the Hydroquinone.—To a solution of 0.50 g. of the 5-trityl-2-(*p*-tolylhydroquinone) in 100 ml. of acetic acid at room temperature, there was added 20 ml. of concentrated nitric acid. The solution immediately became orange colored, and the addition of 400 ml. of water knocked out an orange solid. Recrystallization from 20 ml. of methanol yielded 0.28 g. of orange crystals of the quinone, m.p. 194–195° with softening at 182°; yields, 56%.

Anal. Calcd. for $C_{26}H_{20}O_2$: C, 85.69; H, 5.53. Found: C, 85.82; H, 5.68.

The quinone was quickly and easily reduced to the hydroquinone by extraction of an ether solution (100 mg. in 40 ml. of ether) with three 100-ml. portions of saturated solution of sodium hydrosulfite. The colorless ether layer was evaporated to dryness and the residual oil induced to crystallize by the addition of a drop of toluene. The white solid so obtained (88 mg.) had an infrared scan and melting point identical to the parent hydroquinone from which the quinone had been prepared.

From the Aminophenol.—The aminophenol, 4-amino-5-methyl-2-tritylphenol, was converted to the correspondingly substituted benzoquinone with concentrated nitric acid in glacial acetic acid in exactly the same manner as described above for the hydroquinone oxidation. From 0.5 g. of the amino derivative, there was obtained, after recrystallization from methanol, 0.32 g. of the quinone, m.p. 194–195°, identical in all respects to that obtained by the oxidation of the hydroquinone; yield, 64%.

5-Ethyl-α,α,α-triphenyl-2-cresol: 2-Trityl-5-ethylphenol. Procedure A. Tritylation of *m*-Ethylphenol.—After 2 days, the initial reaction product was removed by filtration and discarded, the mother liquors being allowed to stand. An additional 7 days afforded a moderately heavy crystallization of product which was removed by filtration, and sparingly washed with acetic acid. This product (3.0 g. from 10 g. of phenol, m.p. 135–160°) was a mixture of 2-trityl-5-ethylphenol and 2,4-ditrityl-5-ethylphenol. The monotrityl component could be removed by virtue of its comparatively high solubility in methanol. Evaporation of the methanol extract and treatment of the residual oil with acetic acid yielded a white granular solid which has recrystallized (slowly) from aqueous ethanol. Yield, 7%, of the title compound, m.p. 154–155°.

The dilute carbon tetrachloride infrared spectrum of this material showed almost exclusive OH absorption in a bonded configuration (similar to the *o*-tritylation product of *m*-cresol) establishing that the trityl group had substituted *ortho* to the phenolic hydroxyl group despite the use of the *para* tritylation procedure (procedure A).

Anal. Calcd. for $C_{27}H_{24}O$: C, 88.97; H, 6.64. Found: C, 89.12; H, 6.71.

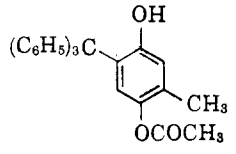
The methanol insoluble material was most easily recrystallized from ethyl acetate yielding the ditrityl homolog as a fine white crystalline powder, m.p. 230–231° (Yield 55%).

Anal. Calcd. for $C_{46}H_{38}O$: C, 91.05; H, 6.31; mol. wt., 607. Found: C, 90.92; H, 6.21; mol. wt., 586 (in MEK).

The configuration (2,4-ditrityl) is preferred to the 2,6-assignment, because of the presence of a small but distinct unbonded —OH isomer (in dilute CCl_4) requiring that an open *ortho* position be available.[20]

Procedure B.—After 3 days heating at 100°, the coal-black reaction product was allowed to crystallize slowly at room temperature. The black sticky crystals were sucked free of unchanged starting phenol and recrystallized (with norite) from aqueous ethanol. There resulted a 52% yield of 2-trityl-5-ethylphenol identical to that prepared in the above-described procedure A.

(19) In some runs, for unestablished reasons, the above product was obtained from the reaction solution with a broad melting point about 30° low. The impurity was assumed to be 4-acetoxy-2-trityl-5-cresol from the spectral change in the infrared in dilute carbon tetrachloride solution—i.e., the disappearance of unbonded



—OH (~3618 cm.$^{-1}$), the retention of trityl-bonded —OH (~3550 cm.$^{-1}$) and the appearance of an esterlike carbonyl absorption at 1764 cm.$^{-1}$. The isolation of this contaminant was not pursued since it could invariably be removed by crystallization from toluene as described above.

(20) A lateral tritylation product is also allowable by the above data—*i.e.*,