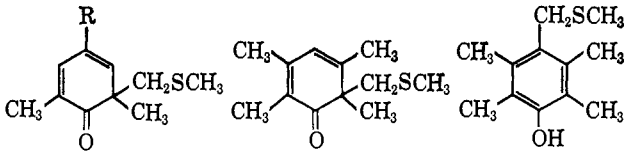
We also consider the observed *meta* and *para* alkylations to be intramolecular. This stems from our inability to detect any alkylation of large excesses of anisole, N,N-dimethylaniline, or furan present during *para* alkylation of 2,6-dimethylphenol. It is likely that both *meta* and *para* alkylation proceed *via* a cyclohexadienone (XIII). In support of this we have found that 2,3,5,6-tetramethylphenol reacts to give a good yield of XIV (λ_{max}^{MeOH} 325 mμ (ϵ 4,600); $\nu_{max}^{CHCl_3}$ 1640 and 1660 cm.$^{-1}$) as a distillable oil with the expected n.m.r. spectrum. Mild acidic treatment of XIV results in its rapid rearrangement to the *para*-alkylated phenol XV, m.p. 144–145°. Desulfurization of the latter gave 2,3,4,5,6-pentamethylphenol (m.p. 126–128°) identical with an authentic sample. If in XIII R = CH_3, however, a dienone–phenol type of arrangement similar to that observed with 6,6-dimethylcyclohexa-2,4-dien-1-one itself[8] can lead to the *meta*-alkylated phenol VIb.



XIII XIV XV

Further studies designed to cast light upon the mechanism of these reactions are in progress.

(8) (a) E. N. Marvel and E. Magoon, *J. Am. Chem. Soc.*, 77, 2542 (1955); (b) H. Budzikiewicz, *Tetrahedron Letters*, 12 (1960).
(9) Receipt of a travel grant from the Welcome Trust is gratefully acknowledged.

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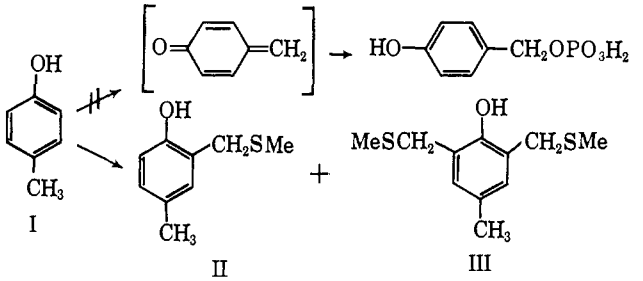
The Reactions of Phenols with Oxysulfonium Cations

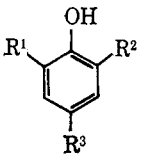
Sir:

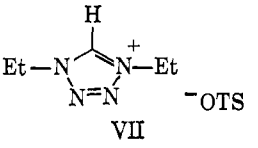
Several procedures for the oxidation of alcohols to aldehydes or ketones *via* oxysulfonium intermediates (ROS^+R_2) are known. These include: (1) reaction of the derived tosylate with dimethyl sulfoxide (DMSO) at high temperature,[1] (2) reaction of the alcohol with DMSO and dicyclohexylcarbodiimide (DCC) in the presence of a proton donor,[2] (3) reaction of the derived chloroformate with DMSO,[3] and (4) reaction of the derived alkoxide with a dimethylmethoxysulfonium salt.[4] In the present communication we wish to describe a few of the contents of a Pandora's box of new reactions and rearrangements discovered in an attempt to extend some of these oxidation procedures to vinylogous alcohols.[5] In particular we hoped to accomplish the transformation of *p*-cresol *via* a postulated quinonoid intermediate to *p*-hydroxybenzyl phosphate by treatment of I with DMSO, DCC, and H_3PO_4. The reaction however took a different course, and the major phenolic products are the thiomethoxymethyl compounds (II and III).[6]



I II III

From *o*-cresol we obtained a 65% yield of the 6-thiomethoxymethyl derivative (IV) and from phenol itself both V and VI were isolated. The highest yields (3 equiv. of DCC) of V (30%) and VI (18%) were





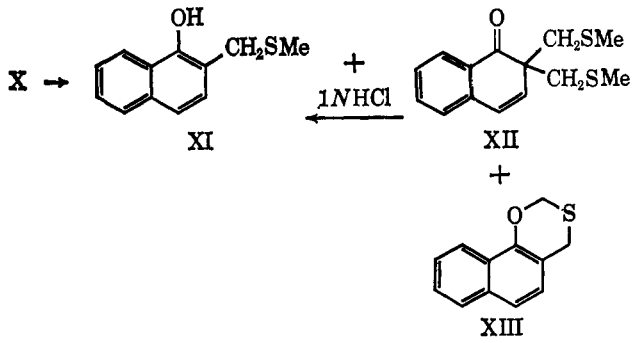
VII

IV, R^1 = Me, R^2 = CH_2SMe, R^3 = H
V, R^1 = CH_2SMe, R^2 = R^3 = H
VI, R^1 = R^2 = CH_2SMe, R^3 = H
VIII, R^1 = COH, R^2 = CH_2SMe, R^3 = H
IX, R^1 = R^2 = Me, R^3 = CH_2SMe

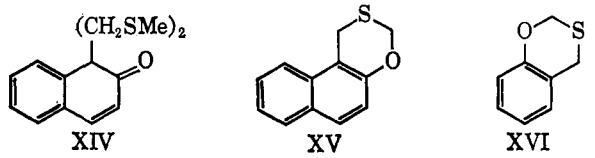
obtained when pyridinium trifluoroacetate (0.5 equiv.) was used as the proton source, though under these conditions N-trifluoroacetyl-N,N′-dicyclohexylurea (m.p. 137–139°) and cyclohexyltrifluoroacetamide (m.p. 93–94°) were also isolated. Similar products are formed from other phenols, other sulfoxides with α-hydrogens, and other carbodiimides (*o*-cresol also gives IV on treatment with 1,4-diethyltetrazolium tosylate (VII) (an *in situ* source of carbodiimide[7]), Et_3N, and H_3PO_4 in DMSO). Salicylaldehyde in addition to yielding the expected *ortho* alkylation product (VIII, 18%) gave the decarbonylated species (V, 16%).

No isomers substituted *para* to the OH could be detected in these reaction mixtures, but, when the *ortho* positions are blocked as in 2,6-dimethylphenol, the *para* product (IX) is encountered in variable yield. Surprisingly, both α-naphthol (X) and β-naphthol yielded conjugated ketones and other extraordinary compounds in addition to the anticipated products. Compounds with the previously unknown 1,3-benzoxathian ring system (as in XIII and XV) are also formed in trace amounts from the simpler phenols including phenol itself, which gives XVI in 2% yield. *o*-Nitrophenol and the other nitrophenols yield oxygen alkylation products like XVII (5%) in addition to compounds of the types already described.

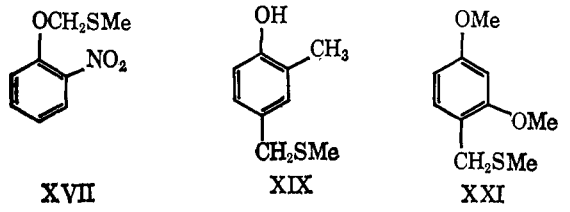
(1) N. Kornblum, W. J. Jones, and G. J. Anderson, *J. Am. Chem. Soc.*, 81, 4113 (1959).
(2) K. E. Pfitzner and J. G. Moffatt, *ibid.*, 85, 3027 (1963).
(3) D. H. R. Barton, B. J. Garner, and R. H. Wightman, *J. Chem. Soc.*, 1855 (1964).
(4) C. R. Johnson and W. G. Phillips, *Tetrahedron Letters*, 2101 (1965).
(5) M. G. Burdon and J. G. Moffatt have independently discovered similar reactions, and simultaneous publication has been arranged (*J. Am. Chem. Soc.*, 87, 4656 (1965)).
(6) The structures of the new compounds described in this communication were determined from a study of their infrared, ultraviolet (neutral and base), and n.m.r. spectra (see Table I), mass spectral fragmentation patterns, and by Raney nickel desulfurization (usually in almost quantitative yield) to the expected known products. Correct elemental analyses were obtained. The products were isolated by extraction followed by distillation or crystallization or, when necessary, preparative layer chromatography.
(7) R. A. Olofson, W. R. Thompson, and J. S. Michelman, *J. Am. Chem. Soc.*, 86, 1865 (1964).



	XI	XII	XIII
a[8]	trace	56%	2.5%
b[8]	16%	43%	5.7%



(both from β-naphthol)



o-Cresol was treated with dimethylethoxysulfonium fluoroborate (XVIII) (m.p. 39–42°, hygroscopic) and Et_3N in CH_2Cl_2 with the expectation that the phenol would displace the ethoxy function[4,9] and that the *ortho*-alkylation product (IV) would be obtained. However, though some IV is isolated, the *major* product is the *para* isomer (XIX). Also, treatment of resorcinol dimethyl ether (XX) with XVIII and Et_3N under the same conditions yields a mixture of compounds from which the alkylated product (XXI) has been isolated and identified. However, XX does *not* react with DCC in DMSO.

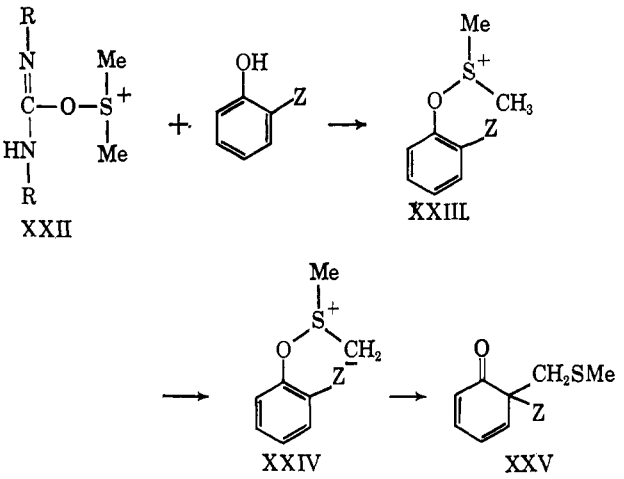
We believe the DCC reactions are related to the Sommelet rearrangement.[10] DCC (activated by H^+) reacts with DMSO to give the isourea (XXII) which is attacked by the phenol to yield the phenoxysulfonium cation (XXIII). This species loses a proton to generate the sulfonium ylid[11] (XXIV) which then undergoes an intramolecular rearrangement to the *ortho* position. Depending on Z the resulting dienone (XXV) may be isolated, it may tautomerize to the phenol (Z = H), Z (=COH) may be removed, or $CH_2{=}S^+{-}Me$ (XXVI) may be eliminated. We suggest XXVI (whether from XXV, XXIV, XXII, or XVIII) is responsible for *para* alkylation, oxygen alkylation, and the reactions of XVIII. The 1,3-benzoxathians probably result from the reaction of XXII with XXIII

(8) a, H_3PO_4 catalyst; b, pyridinium trifluoroacetate catalyst.
(9) C. R. Johnson, *J. Am. Chem. Soc.*, **85**, 1020 (1963).
(10) H. E. Zimmerman in "Molecular Rearrangements," P. de Mayo, Ed., Interscience Publishers, Inc., 1963, pp. 345–406.
(11) Me_3S^+ is easily exchanged in D_2O–base (W. von E. Doering and A. K. Hoffman, *J. Am. Chem. Soc.*, 77, 521 (1955)). The replacement of a methyl by the electron-withdrawing phenoxy should enhance the acidity of the methyl protons by several powers of ten (ref. 7 and unpublished results).

Table I. N.m.r. Spectra of New Compounds

Compd.	M.p. or b.p., °C. (mm.)	N.m.r. (τ) in CCl_4
II	Oil	3.09–3.44 (m), 6.39 (s), 7.82 (s), 8.12 (s); 4:2:3:3
III	Oil	3.05–3.30 (m), 6.37 (s), 7.82 (s), 8.09 (s); 3:4:3:6
IV	71 (0.4)	3.00–3.41 (m), 3.53 (s), 6.41 (s), 7.83 (s), 8.19 (s); 3:1:2:3:3
V	73–74 (0.3)	2.83–3.44 (m), 6.38 (s), 8.12 (s); 5:2:3
VI	119–120 (0.3)	2.90–3.44 (m), 6.34 (s), 8.12 (s); 4:4:6
VIII	Oil	−1.28 (s), 0.26 (s), 2.50–3.26 (m), 6.36 (s), 8.04 (s); 1:1:3:2:3
IX	41–43	2.92 (s), 3.29 (s), 6.60 (s), 7.86 (s), 8.13 (s), 8.13 (s); 1:2:2:6:3
XI	Oil	2.32–3.13 (m), 6.29 (s), 8.22 (s); 7:2:3
XII	Oil	1.96–2.89 (m), 3.28 (d), 3.88 (d), 7.12 (s), 8.04 (s); 4:1:1:4:6
XIII	62	1.83–3.21 (m), 4.72 (s), 6.19 (s); 6:2:2
XIV	69–71	2.51–2.77 (m), 3.79 (d), 6.98 (s), 8.20 (s); 5:1:4:6
XV	65–66	2.29–3.13 (m), 4.90 (s), 6.01 (s); 6:2:2
XVI	Oil	2.99–3.33 (m), 4.88 (s), 6.25 (s); 4:2:2
XVII	Oil	2.17–3.14 (m), 4.77 (s), 7.75 (s); 4:2:3
XIX	Oil	3.10–3.58 (s), 6.52 (s), 7.83 (s), 8.11 (s); 4:2:3:3
XXI	Oil	2.76–3.78 (m), 6.28 (s), 6.32 (s), 6.46 (s), 8.09 (s); 3:3:3:2:3

or another sulfonium ylid. Further studies designed to clarify the mechanisms of these reactions are in progress.



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