provide routes to *nucleophilic acylations* of electrophiles other than the proton, provided the latter is not readily available. We have demonstrated the utility of this concept for the establishment of carbon–carbon bonds by performing the nucleophilic benzoylation of benzoic anhydride. The reaction of the tetramethylammonium salt of I with benzoic anhydride and pyridine in refluxing mesitylene produced a 40% yield of benzil.[2,20]

(20) No attempt was made to optimize yields.

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## The Alkaline Hydrolysis of Catechol Cyclic Sulfate. An Extraordinary Rate Acceleration

Sir:

For many years it has been known that five-membered cyclic esters of phosphoric acid are intermediates in the hydrolysis of ribonucleic acids.[1] Although most diesters of phosphoric acid are relatively resistant to alkaline hydrolysis, these cyclic phosphoric acid esters are rapidly hydrolyzed.[1,2] Studies on the simplest cyclic ester of phosphoric acid, ethylene phosphate, revealed that its salts hydrolyze in alkali at about 10^7 times the rate observed for the corresponding salts of the open chain compound, dimethyl phosphate.[3,4] The alkaline hydrolysis of ethylene phosphate has been demonstrated to occur exclusively with P–O bond cleavage, whereas dimethyl phosphate hydrolyzes in large part with C–O bond cleavage.[5,6] As a result of this difference in the modes of bond cleavage, the rate enhancement for attack at phosphorus by hydroxide ion is estimated to be greater than 10^8. Further studies have shown that this large rate enhancement is not unique for five-membered cyclic esters of phosphoric acid. The five-membered cyclic ester of phosphonic acid, lithium propylphostonate, is hydrolyzed 10^6 times as fast as the open chain compound, sodium ethyl ethylphosphonate.[7]

In an attempt to elucidate the unusual behavior of the five-membered cyclic esters of phosphoric acid, the hydrolysis of ethylene sulfate was investigated and compared to that of dimethyl sulfate. Ethylene sulfate was found to hydrolyze in alkaline solution only slightly faster than dimethyl sulfate.[8] However, whereas ethylene sulfate hydrolyzes with about 14% S–O bond cleavage in alkali, dimethyl sulfate is hydrolyzed exclusively *via* attack at carbon with concomitant C–O bond cleavage. Therefore it was not possible to measure the relative rate factor for attack

at sulfur in these compounds, and the question whether the kinetic acceleration at sulfur in the five-membered ring compound is large remained unsolved.

The present communication reports a kinetic study of the alkaline hydrolysis of the five-membered cyclic sulfate, catechol cyclic sulfate (I), and its open chain analog, diphenyl sulfate (II). Nucleophilic attack of hydroxide ion at the aromatic carbon atoms in these compounds should be extremely unlikely. Thus, the difference in the rate of hydrolysis of the two esters should represent the difference in the rate of attack of
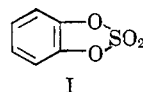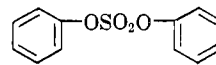
hydroxide ion at sulfur for a five-membered cyclic sulfate compared to that for its open-chain analog.

Catechol cyclic sulfate (I), m.p. 34–35°, was prepared in low yield from the reaction of catechol with sulfuryl chloride in petroleum ether in the presence of pyridine.[9] *Anal.* Calcd. for $C_6H_4O_4S$: C, 41.86; H, 2.33; S, 18.60. Found: C, 41.68; H, 2.18; S, 18.53. On alkaline hydrolysis of I the monoester, 2-hydroxyphenyl sulfate, is produced. Measurements with a Radiometer Type TTT1b titrator in conjunction with a Type SBR2C titrigraph and GK 2021 C electrode gave a second-order rate constant of 18.8 M^{-1} sec.$^{-1}$ for the alkaline hydrolysis of I at 25.0°.

Diphenyl sulfate (II), b.p. 95–97° (0.05 mm.), was obtained by allowing a mixture of phenol, pyridine, and sulfuryl chloride to react at low temperature in petroleum ether.[10] *Anal.* Calcd. for $C_{12}H_{10}O_4S$: C, 57.59; H, 4.03; S, 12.81. Found: C, 57.70; H, 4.20; S, 12.97. Alkaline hydrolysis of II led to the formation of the monoester, phenyl sulfate, and of phenol. The hydrolytic reactions were conducted in brass-enclosed Teflon reaction cells placed in a thermostated oil bath, and the rates of hydrolysis were determined by quantitative vapor phase chromatographic analysis of unreacted II as a function of time. Values of 13 × 10^{-6}, 30 × 10^{-6}, and 178 × 10^{-6} M^{-1} sec.$^{-1}$ were found for the second-order rate constants for the alkaline hydrolysis of II at 50.0, 60.0, and 80.0°, respectively. Extrapolation of these results to 25.0° gave a value for the second-order rate constant of 8.9 × 10^{-7} M^{-1} sec.$^{-1}$.

Thus, comparison of the relative rate constants observed for the alkaline hydrolysis of catechol cyclic sulfate and diphenyl sulfate, which reflects the difference in the rate of attack by hydroxide ion at sulfur in these two compounds, shows that the five-membered cyclic diester hydrolyzes 2 × 10^7 times faster than its open chain analog.[11] This represents the first observa-

(1) R. Markham and J. D. Smith, *Biochem. J.*, **52**, 552 (1952); D. Lipkin, P. T. Talbert, and M. Cohn, *J. Am. Chem. Soc.*, **76**, 2871 (1954); A. Fono, *Archiv. Kemi Mineral. Geol.*, **24A**, 34, 19 (1947); D. M. Brown and A. R. Todd, *J. Chem. Soc.*, 52 (1952).

(2) D. M. Brown, D. I. Magrath, and A. R. Todd, *ibid.*, 2708 (1952); T. Ukita, N. A. Bates, and H. E. Carter, *J. Biol. Chem.*, **216**, 867 (1955).

(3) J. Lecocq, *Compt. rend.*, **242**, 1902 (1956).

(4) J. Kumamoto, J. R. Cox, Jr., and F. H. Westheimer, *J. Am. Chem. Soc.*, **78**, 4858 (1956).

(5) C. A. Bunton, D. R. Llewellyn, K. G. Oldham, and C. A. Vernon, *J. Chem. Soc.*, 3574 (1958).

(6) P. Haake and F. H. Westheimer, *J. Am. Chem. Soc.*, **83**, 1102 (1961).

(7) A. Eberhard and F. H. Westheimer, *ibid.*, **87**, 253 (1965).

(8) E. T. Kaiser, M. Panar, and F. H. Westheimer, *ibid.*, **85**, 602 (1963).

(9) The preparation of I has been reported by L. Denivelle in *Compt. rend.*, **203**, 194 (1936), but we were unable to repeat his procedure nor were we able to reproduce the melting point (47°) which he obtained for this compound. The n.m.r. and infrared data which we determined were in accord with structure I.

(10) L. Denivelle, *ibid.*, **199**, 211 (1934); L. Bollinger, *Bull. soc. chim. France*, 156 (1948); H. Geis and E. Pfeil, *Ann.*, **578**, 11 (1952).

(11) The largest rate difference found previously in sulfur-containing systems was that between the alkaline hydrolysis of catechol cyclic sulfite and diphenyl sulfite, the five-membered cyclic ester hydrolyzing only 1.5 × 10^3 times more rapidly than its open chain analog (P. De la Mare, J. Tillett, and H. van Woerden, *J. Chem. Soc.*, 4888 (1962)). Cyclic sulfites differ considerably from cyclic sulfates in their hydrolytic behavior. For example, ethylene sulfate releases about 6 kcal./mole more heat on hydrolysis than does dimethyl sulfate, but the heats of hydrolysis of ethylene sulfite and dimethyl sulfite are nearly the same (see ref. 8 and a paper by R. E. Davis in *J. Am. Chem. Soc.*, **84**, 599 (1962)).

tion of such an enormous rate enhancement for the hydrolysis of a five-membered cyclic ester which contains a heteroatom other than phosphorus. The origin of the extraordinary lability of catechol cyclic sulfate is now under study.

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Photorearrangement of Di-t-butyl-p-benzoquinones

Sir:

The current general interest in the photochemistry of carbonyl compounds has recently been extended to studies involving several p-benzoquinone systems. Some early work demonstrated the photoreduction of p-benzoquinone to hydroquinone in alcoholic solvents.[1] More recently, photodimerization[2] of some substituted p-benzoquinones and photocycloaddition with olefins[3] has been observed. We wish to report here the photorearrangement of the di-t-butyl-p-benzoquinones Ia and Ib in alcohol solution.
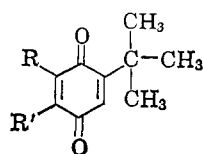
Ia, R = t-Bu; R' = H
b, R = H; R' = t-Bu

Photolysis[4] of a 0.2 M solution of Ia in ethanol for 24 hr. at 25–30° resulted in the isolation of an orange-red oil after solvent evaporation. Trituration of this oil with hexane provided a crystalline, white solid, 2.0 g. (38%), m.p. 128–130° (from hexane–benzene). Elemental analysis (*Anal.* Calcd. for $C_{16}H_{26}O_3$: C, 72.10; H, 9.77. Found: C, 71.50; H, 9.92) and mass spectral determination of the molecular weight (mol. wt. 266) showed that this product (II) was a 1:1 adduct of the quinone and ethanol. An analogous product (III), m.p. 119.6–121.6°, was obtained in 50% yield when methanol was substituted for ethanol.

The infrared spectrum [λ_{max}, μ: 2.97 (s), 3.17 (s) (OH); 6.24 (m) (aromatic C=C); 9.02 (s), 9.46 (s) (–C–O–C–)] and the ultraviolet spectrum [λ_{max}^{THF}, mμ: 238 (ϵ 16,000); 297 (ϵ 47,500)] were indicative of a hindered phenolic system.[5] The n.m.r. spectrum provided confirmation for this structure: a broad peak at τ 5.0 (1 H) and a sharp singlet at τ 1.25 (1 H) found in the spectrum of IIa which disappeared on the addition of D_2O to the $CDCl_3$ solution pointed to the presence of one unhindered and one severely hindered hydroxyl group. Evidence for two mutually coupled aromatic protons

(1) (a) P. A. Leighton and G. S. Forbes, *J. Am. Chem. Soc.*, **51**, 3546 (1929); (b) A. Schönberg and A. Mustafa, *Chem. Rev.*, **40**, 181 (1947).
(2) (a) R. C. Cookson and J. Hudec, *Proc. Chem. Soc.*, 11 (1959); (b) E. Zavarin, *J. Org. Chem.*, **23**, 47 (1958); (c) R. C. Cookson, D. A. Cox, and J. Hudec, *J. Chem. Soc.*, 4499 (1961); (d) D. Bryce-Smith and A. Gilbert, *ibid.*, 2428 (1964).
(3) (a) D. Bryce-Smith and A. Gilbert, *Proc. Chem. Soc.*, 87 (1964); (b) D. Bryce-Smith and A. Gilbert, *Tetrahedron Letters*, 3471 (1964); (c) G. O. Schenck, I. Hartmann, and W. Metzner, *ibid.*, 347 (1965).
(4) Photolysis was carried out using a Pyrex vessel and a 275-w. G.E. sunlamp.
(5) C. D. Cook, R. G. Inskeep, A. S. Rosenberg, and E. C. Curtius, Jr., *J. Am. Chem. Soc.*, **77**, 1672 (1955).

was supplied by a pair of doublets (AB pattern) at τ 3.15 and 3.48. A quartet at τ 6.47 (J = 8.5 c.p.s., 2 H) and a triplet at 8.77 (J = 8.5 c.p.s., 3 H) constituted a clear indication for an ethoxy group. Taking into account the presence of two phenolic hydroxy groups, two aromatic protons, and two side chains, it became apparent that the ethoxy group could not be attached directly to the aromatic ring. Support for this conclusion was provided by the observation that two singlets at τ 8.40 (9 H) and 8.77 (6 H) account for only five of the six methyl groups that were present in Ia. A singlet was found at τ 7.20 (2 H) which signified that one of the original methyl groups had been converted into a methylene group. Hence, the adduct must be a hydroquinone which has one t-butyl side chain and one other side chain that contains an ethoxy group. Two reasonable structures (IIa and IIb) can be written for the adduct at this stage.
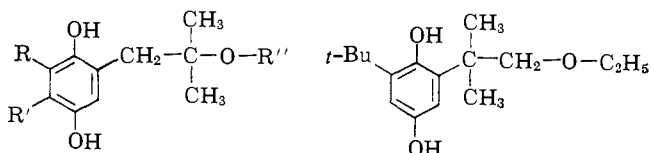
IIa, R = t-Bu; R' = H; R'' = C_2H_5 IIb
III, R = t-Bu, R' = H; R'' = CH_3
IV, R = H; R' = t-Bu; R'' = C_2H_5
V, R = H; R' = $CH_2C(CH_3)_2OC_2H_5$;
        R'' = C_2H_5

Further structural information was sought by the acetylation and oxidation of II. Treatment with acetic anhydride–pyridine converted II into a monoacetate[6] (VI), m.p. 63.5–65.5°. The n.m.r. spectrum of VI showed a sharp peak at τ 1.58 which disappeared very slowly on the treatment of a $CDCl_3$ solution of VI with D_2O. This behavior is in keeping with the hindered position of one of the hydroxyl groups in II.

Oxidation of II at 25° with chromic acid in acetic acid[7] led to the quinone[6] VII as a liquid. The n.m.r. spectrum of VII was very similar to that of II except in the aromatic region: in place of the distinct AB quartet of II there appeared one signal (2 H) of complex pattern centered at τ 3.00. This complexity must be caused by additional coupling through long-range spin–spin interaction. In structure VII the methylene group should undergo allylic coupling with the nearer of the two aromatic protons which are mutually coupled through the ketone. In the alternative structure (corresponding to IIb) neither allylic nor homoallylic coupling (H—C—C=C—C—H) is feasible. Irradiation of the methylene signal at τ 7.20 caused the multiplet at 3.00 in the high-frequency side band to resolve into a quartet (AB pattern), whereas irradiation of the τ 3.00 signal with the same decoupling frequency caused a sharpening of the methylene peak at 7.20 in the low-frequency side band. This double resonance experiment shows that the methylene group is coupled (J < 1 c.p.s.) with one of the aromatic protons and thus supports the structure VII. The coupling between the two aromatic protons (J = 2.9 c.p.s.) is consistent with their *meta* relationship to each other. If the molecular rearrangement had involved the migration of the side chain from one nuclear

(6) Satisfactory microanalyses were obtained for this compound.
(7) C. F. Koelsch and S. Wawzonek, *J. Am. Chem. Soc.*, **65**, 755 (1943).