

**Acknowledgment.** E.J. wishes to express his gratitude to Professor Ernest L. Eliel for many helpful discussions and for a careful reading of this manuscript.

**Registry No.** 1, 505-23-7; 1-*d*, 14664-88-1; 1-Li, 53178-41-9; 2, 5425-44-5; 2-*d*, 74447-48-6; 2-Li, 36049-90-8; 3-Li, 60349-88-4; 4, 98-53-3; 4-*d*, 2979-37-5; 5, 92787-88-7; 6, 92787-89-8; 7, 17181-

81-6; 8, 17181-80-5; 9, 566-88-1; 10, 19490-62-1; 12, 40615-42-7; 13, 40615-41-6; 14, 16980-55-5; 15, 16980-56-6; 16, 92787-90-1; 17, 92787-91-2; 18, 92787-92-3.

**Supplementary Material Available:**  $^{13}\text{C}$  chemical shift data for 5-8, 12, 13, and 18 (2 pages). Ordering information is given on any current masthead page.

## Sulfonation of Three Symmetrical 2,6-Dialkylphenols, 2,6-Dichlorophenol, Phenol, and 2,6-Dimethylanisole. Sulfation and Sulfonation Product Distributions and Mechanisms<sup>1</sup>

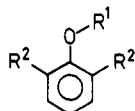
Hans Cerfontain,\* Ankie Koeberg-Telder, Hans J. A. Lambrechts,<sup>†</sup> and Peter de Wit

Laboratory for Organic Chemistry, University of Amsterdam, Nieuwe Achtergracht 129, 1018 WS Amsterdam, The Netherlands

Received March 22, 1984

The sulfonation of four symmetrically 2,6-disubstituted phenols, phenol, and 2,6-dimethylanisole with  $\text{SO}_3$  in aprotic solvents was studied. With the phenols the initial product is the phenyl hydrogen sulfate, which is slowly converted into the phenolsulfonic acids via O-desulfonation and subsequent C-sulfonation if the phenol is in excess and via C-sulfonation and subsequent O-desulfonation if the  $\text{SO}_3$  is in excess. The ratio of partial rate factors for 3- and 4-sulfonation ( $f_3/f_4$ ) for 2,6-dimethylphenol (1) in nitromethane strongly decreases on replacing the methyl groups by *i*-Pr, *t*-Bu (steric effects), and Cl (electronic effects). The strong increase of  $f_3/f_4$  on increasing the  $\text{SO}_3$ :1 ratio from 0.9 to 6.0 is ascribed to increasing sulfonation of the phenyl hydrogen sulfate for which because of steric inhibition of resonance  $f_3/f_4$  is higher (3.9) than that of the phenol 1 (<0.01) and of 2,6-dimethylanisole (5) (<0.01). The protic sulfonation of 1 and 5 in concentrated sulfuric acid was also studied. The large variations in  $f_3/f_4$  with increasing sulfuric acid concentration are discussed in terms of steric inhibition of resonance for the entities undergoing sulfonation, viz., 1, its hydrogen sulfate, and 5 by the various sulfonating entities in the sulfuric acid range 75-107%  $\text{H}_2\text{SO}_4$ .

Recently Miller et al. reported that the benzylation of 2,6-dimethylphenol (1) and its methyl ether (5) yields in



- 1  $\text{R}^1 = \text{H}$ ;  $\text{R}^2 = \text{Me}$
- 2  $\text{R}^1 = \text{H}$ ;  $\text{R}^2 = \text{Pr}^i$
- 3  $\text{R}^1 = \text{H}$ ;  $\text{R}^2 = \text{Bu}^t$
- 4  $\text{R}^1 = \text{H}$ ;  $\text{R}^2 = \text{Cl}$
- 5  $\text{R}^1 = \text{R}^2 = \text{Me}$
- 6  $\text{R}^1 = \text{R}^2 = \text{H}$
- 7  $\text{R}^1 = \text{Me}$ ;  $\text{R}^2 = \text{H}$

addition to the expected 4-benzyl derivative substantial amounts of the 3-benzyl derivative (ca. 40% and 70% respectively),<sup>2</sup> and further that the allylation of these substrates also leads to both 3- and 4-substitution.<sup>3</sup> A search of the literature failed to reveal a single instance of an electrophilic substitution reaction of a simple phenol or aryl ether with unsubstituted positions ortho or para to the oxygen atom in which significant amounts of meta substitution occurred.<sup>2</sup> Most of the cited literature is rather outdated and not always conclusive. For instance, the sulfonation of 1 with 85% sulfuric acid<sup>4</sup> and its nitration with 80% nitric acid<sup>5</sup> led to the 4-substituted product in isolated yields of only ca. 40% and 50%, respectively.

2,6-Dialkylphenols and their methyl ethers are intriguing, as they may be considered both as a phenol and its ether (for which the electrophilic substitution is strongly directed to the 2- and 4-positions) and as a *m*-dialkylbenzene (which directs strongly to the 3-position). The substituent constant  $\sigma^+$  for substitution para to the OH and OMe substituents are -0.92 and -0.78, respectively,<sup>6</sup> whereas the overall substituent constant for substitution at the 4-position of *m*-xylene is  $\sigma^+_{\text{O-Me}} + \sigma^+_{\text{p-Me}} = -0.197 + -0.286 = -0.47$ . Thus with the 2,6-dimethyl derivatives of phenol and anisole the effects of the OH and OMe substituents strongly dominate over the directing effect of the two methyls provided that the former substituents can fully exert their conjugative effect, i.e., that the OH hydrogen and the OMe carbon are in the plane of the phenyl ring. Any torsion of the OH and OMe substituents because of steric hindrance with the adjacent alkyl groups will reduce the mesomeric conjugation between the OH and OMe substituents and the cationic cyclohexadienyl structure in the transition state that leads to 4-substitution. This will then allow the much slower 3-substitution to become a competing reaction.

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<sup>†</sup> Present address: Quaker Chemical (Holland) B.V., Industrieweg 3-13, 1422 AH Uithoorn, The Netherlands

Table II. Sulfonation of 1-6 with SO<sub>3</sub>

| entry | no. | method <sup>a</sup> | SO <sub>3</sub> , equiv | reactn time, min | unconverted substrate, % | products, %        |                     |                     |                                      |
|-------|-----|---------------------|-------------------------|------------------|--------------------------|--------------------|---------------------|---------------------|--------------------------------------|
|       |     |                     |                         |                  |                          | OSO <sub>3</sub> H | 3-SO <sub>3</sub> H | 4-SO <sub>3</sub> H | 4,O-(SO <sub>3</sub> H) <sub>2</sub> |
| 1     | 1   | A                   | 1.0                     | 10               | <1                       | >99                |                     |                     |                                      |
| 2     | 1   | B                   | 1.0                     | 7 <sup>b</sup>   | 18                       | 69                 |                     | 31 <sup>b</sup>     |                                      |
| 3     | 1   | D                   | 0.9                     | 30               | nd                       |                    |                     | >98                 |                                      |
| 4     |     | D                   | 1.3                     | 30               | nd                       |                    | 4                   | 96                  |                                      |
| 5     |     | D                   | 1.7                     | 30               | nd                       |                    | 4 <sup>c</sup>      | 87                  | 6                                    |
| 6     |     | D                   | 2.0                     | 30               | nd                       |                    | 11 <sup>c</sup>     | 83                  | 3                                    |
| 7     |     | D                   | 3.0                     | 30               | nd                       |                    | 35 <sup>d</sup>     | 60                  | 2.5                                  |
| 8     |     | D                   | 4.0                     | 30               | nd                       |                    | 65 <sup>e</sup>     | 35                  | <2                                   |
| 9     |     | D                   | 5.0                     | 30               | nd                       |                    | 67 <sup>e</sup>     | 33                  | <2                                   |
| 10    |     | D                   | 6.0                     | 30               | nd                       |                    | 77 <sup>e</sup>     | 23                  | <2                                   |
| 11    | 2   | A                   | 1.0                     | ca. 15           | 42                       | >99                |                     |                     |                                      |
| 12    |     | A                   | 1.2                     | ca. 15           | 28                       | 99                 |                     |                     |                                      |
| 13    |     | A                   | 1.4                     | ca. 15           | 22                       | 98                 |                     |                     |                                      |
| 14    |     | A                   | 1.9                     | ca. 40           | 3                        | 98                 |                     |                     |                                      |
| 15    |     |                     |                         | 3.5 days         | 16                       | <1                 |                     | >99                 |                                      |
| 16    | 2   | D                   | 1.0                     | 30               | nd                       |                    |                     | >99                 |                                      |
| 17    |     | D                   | 4.0                     | 30               | nd                       |                    |                     | >99                 |                                      |
| 18    | 3   | D                   | 1.0                     | 30               | nd                       |                    |                     | >98                 |                                      |
| 19    |     | D                   | 4.0                     | 30               | nd                       |                    |                     | 16 <sup>f</sup>     |                                      |
| 20    | 4   | B                   | 1.1                     | 15               | <1                       | 99                 |                     |                     |                                      |
| 21    |     | B                   |                         | 2                | <1                       | 98                 |                     | <1                  | 2.2                                  |
| 22    |     | B                   |                         | 22               | <1                       | 72                 |                     | 19                  | 8.6                                  |
| 23    |     | B                   |                         | 27               | <1                       | 64                 |                     | 26                  | 9.2                                  |
| 24    |     | B                   |                         | 65               | <1                       | 42                 |                     | 52                  | 6.1                                  |
| 25    |     | B                   |                         | 80               | <1                       | 31                 |                     | 63                  | 5.6                                  |
| 26    |     | B                   |                         | 95               | <1                       | 26                 |                     | 69                  | 5.0                                  |
| 27    |     | B                   |                         | 115              | <1                       | 19                 |                     | 76                  | 4.1                                  |
| 28    | 5   | D                   | 1.0                     | 30               | nd                       |                    | 3                   | 97                  |                                      |
| 29    | 6   | C                   | 1.2                     | 15               | ≤1                       | >99                |                     |                     |                                      |
| 30    |     | C                   |                         | 70               | ≤1                       | <1                 |                     | 87                  | 13                                   |
| 31    | 6   | C                   | 0.7                     | 15               | 31                       | 77                 |                     | 23                  |                                      |
| 32    |     | C                   |                         | 3                | 31                       | 74                 |                     | 26                  |                                      |
| 33    |     | C                   |                         | 6                | 32                       | 64                 |                     | 36                  |                                      |
| 34    |     | C                   |                         | 8                | 33                       | 56                 |                     | 44                  |                                      |
| 35    |     | C                   |                         | 11               | 31                       | 47                 |                     | 53                  |                                      |
| 36    |     | C                   |                         | 18               | 33                       | 28                 |                     | 72                  |                                      |
| 37    |     | C                   |                         | 25               | 31                       | 22                 |                     | 78                  |                                      |

<sup>a</sup>See Experimental Section. <sup>b</sup>After 10 min the 4-sulfonic acid started to precipitate slowly. <sup>c</sup>Plus 3% of the O-sulfate. <sup>d</sup>Plus 2.5% of the O-sulfate. <sup>e</sup>Plus <2% of the O-sulfate. <sup>f</sup>The principal product was 2-*tert*-butylphenol-2,6-disulfonic acid (84%).

In view of our extensive studies on the sulfonation of both the 1,3-dialkylbenzenes (alkyl = Me,<sup>8</sup> Et,<sup>9</sup> *i*-Pr,<sup>10</sup> and *t*-Bu<sup>11</sup>) and phenol and anisole,<sup>12</sup> we have made a detailed study on the sulfonation of a series of symmetrical 2,6-disubstituted phenols and 2,6-dimethylanisole under both aprotic and protic conditions.

### Results

The aromatic substrates were sulfonated (i) with SO<sub>3</sub> in nitromethane at various temperatures and (ii) in concentrated aqueous sulfuric acid at 25 °C. The amounts of the various sulfonation products in the reaction mixtures were determined by <sup>1</sup>H NMR spectroscopy.<sup>13</sup> The assignments are compiled in Table I (supplementary material). The compositions of the sulfonic acid product mixtures were determined by <sup>1</sup>H NMR multicomponent analysis on the basis of the specific absorption of the various components.<sup>13</sup>

**Sulfonation with SO<sub>3</sub> in Nitromethane and Dioxane.** The results of the sulfonation of the 2,6-disubstituted

Table III. First-Order Rate Constants for the Conversion of Phenyl Hydrogen Sulfate into Phenol-4-sulfonic Acid in Nitromethane-*d*<sub>3</sub> as Solvent at 0 °C

| PhOSO <sub>3</sub> H | initial reactn mixture composition, M |   | 10 <sup>4</sup> k <sub>1</sub> , s <sup>-1</sup> (±10%) |
|----------------------|---------------------------------------|---|---|
|                      | PhOH                                  | 4-HOC <sub>6</sub> H <sub>4</sub> SO <sub>3</sub> H |   |
| 0.34                 | 0.13                                  | 0.041   | 8.8   |
| 0.29                 | 0.17                                  | 0.10  | 10.3  |
| 0.32                 | 0.23                                  | 0.054   | 9.6   |
| 0.14                 | 0.31                                  | 0.11  | 9.5   |
| 0.19                 | 0.33                                  | 0.086   | 10.4  |

substrates 1-5 with SO<sub>3</sub> are collected in Table II. It appears that the initial reaction is oxygen sulfonation, and that the ring sulfonation is a subsequent process. With 2,6-dimethylphenol (1), the ratio of 3- to 4-substitution increases strongly with an increasing amount of SO<sub>3</sub> (entries 3-10). With the 2,6-disubstituted phenols other than 1 and 5 no sulfonation of the 3-position was observed. 2,6-Di-*tert*-butylphenol (3) upon reaction with more than 1 equiv of SO<sub>3</sub> undergoes replacement of one *tert*-butyl group by SO<sub>3</sub>H (entry 19).

For comparison the reaction of phenol (6) with SO<sub>3</sub> in nitromethane-*d*<sub>3</sub> was studied. Reaction with a slightly deficient amount of SO<sub>3</sub> at -35 °C led to the rapid formation of phenyl hydrogen sulfate, which at 0 °C slowly yielded phenol-4-sulfonic acid as the only eventual product. The conversion into the 4-sulfonic acid is first order with respect to the phenyl hydrogen sulfate. The first order rate constant is independent of the concentration of phenol (Table III).

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(9) Koeberg-Telder, A.; Cerfontain, H. *J. Chem. Soc., Perkin Trans. 2* 1977, 717.

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(11) Ris, C.; Cerfontain, H. *J. Chem. Soc., Perkin Trans. 2* 1975, 1438.

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Table IV. Product Distribution in Sulfuric Acid Sulfonation at 25 °C

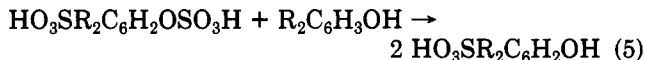
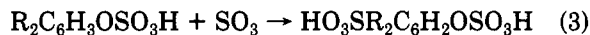
| no. | % H <sub>2</sub> SO <sub>4</sub> | product composition, % |                                      |                     |                                      |
|-----|----------------------------------|------------------------|--------------------------------------|---------------------|--------------------------------------|
|     |                                  | 3-SO <sub>3</sub> H    | O,3-(SO <sub>3</sub> H) <sub>2</sub> | 4-SO <sub>3</sub> H | O,4-(SO <sub>3</sub> H) <sub>2</sub> |
| 1   | 75.0                             | 15                     |                                      | 85                  |                                      |
|     | 80.0                             | 19                     |                                      | 81                  |                                      |
|     | 84.9                             | 25                     | 2                                    | 72                  | 1                                    |
|     | 89.1                             | 28                     | 4                                    | 64                  | 4                                    |
|     | 91.5                             | 30                     | 6                                    | 60                  | 4                                    |
|     | 92.9                             | 30                     | 13                                   | 52                  | 5                                    |
|     | 96.9                             | 20                     | 28                                   | 37                  | 15                                   |
|     | 98.4                             | 13                     | 34                                   | 30                  | 23                                   |
|     | 102.1 <sup>a</sup>               |                        | 52                                   | 3                   | 43                                   |
|     | 105.0 <sup>a</sup>               |                        | 14                                   | 1                   | 46                                   |
|     | 107.3 <sup>a</sup>               |                        |                                      |                     | 53                                   |
| 2   | 98.4                             | ←3→                    |                                      | 57                  | 40                                   |
| 3   | 75.0                             | 50                     |                                      | 50                  |                                      |
|     | 80.0                             | 55                     |                                      | 45                  |                                      |
|     | 84.5                             | 70                     |                                      | 30                  |                                      |
|     | 89.1                             | 78                     |                                      | 22                  |                                      |
|     | 91.5                             | 80                     |                                      | 20                  |                                      |
|     | 92.9                             | 81                     |                                      | 19                  |                                      |
|     | 96.9                             | 81                     |                                      | 19                  |                                      |
|     | 98.4                             | 79                     |                                      | 21                  |                                      |
|     | 102.1 <sup>b</sup>               |                        |                                      |                     | 22                                   |
|     | 107.3 <sup>c</sup>               |                        |                                      |                     | 47                                   |

<sup>a</sup>The O,3,5-trisulfonated derivative was also formed in amounts of 2%, 39%, and 47%, respectively, in order of increasing [H<sub>2</sub>SO<sub>4</sub>].  
<sup>b</sup>The 3,5-disulfonic acid and its O-sulfate comprised 78% of the product. <sup>c</sup>The O,3,5-trisulfonated derivative comprised 53% of the product.

**Sulfonation in Sulfuric Acid at 25 °C.** The sulfonation of 1, 2, and 5 in a very large excess of sulfuric acid was studied at 25 °C. The composition of the reaction mixtures are given in Table IV and the pseudo-first-order rate constants for 1 and 5 in Table V. 2,6-Dimethylphenol (1) and 2,6-dimethylanisole (5) undergo sulfonation at both the 3- and 4-positions and the 3-/4-position ratio increases by factors of 5 and 4 respectively upon increasing the sulfuric acid concentration from 75% to 95%. The ratio of 3- to 4-substitution is independent of the reaction time, illustrating that the product formation is kinetically controlled. The degree of 3-substitution is very much less for 2 than 1.

### Discussion

**Sulfonation with SO<sub>3</sub> in Aprotic Solvents.** The initial reaction is the formation of the phenyl hydrogen sulfate [step 1]. The phenol-3- and -4-sulfonic acids may



be formed from the corresponding phenyl hydrogen sulfates via two routes: first, by regeneration of the phenol and SO<sub>3</sub> and subsequent ring sulfonation [steps -1 and 2], and second, by initial C-sulfonation [step 3] and subsequent O-desulfonation [step 4]. The sulfation of a given phenol is rapid relative to the ring sulfonation of both that phenol ( $k_1 \gg k_2$ ) and its phenyl hydrogen sulfate ( $k_1 \gg k_3$ ),<sup>14</sup> as follows from the studies of 1 in dioxane (Table II,

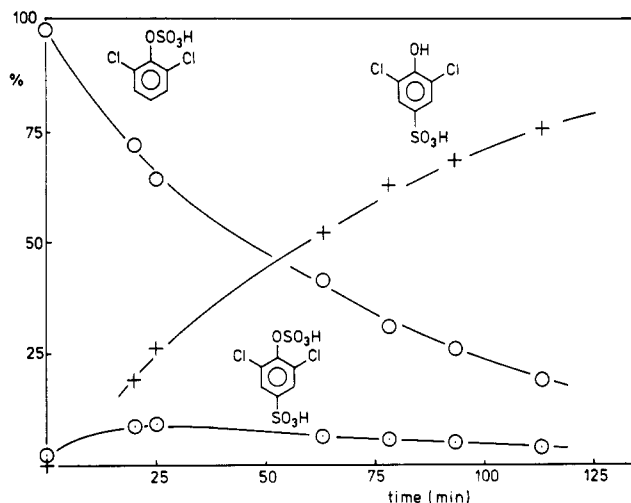


Figure 1. Reaction of 2,6-dichlorophenyl hydrogen sulfate (prepared from 0.50 mmol of 4 with 1.08 equiv of SO<sub>3</sub> in 1.0 mL dioxane-*d*<sub>6</sub> at -30 °C) at 60 °C.

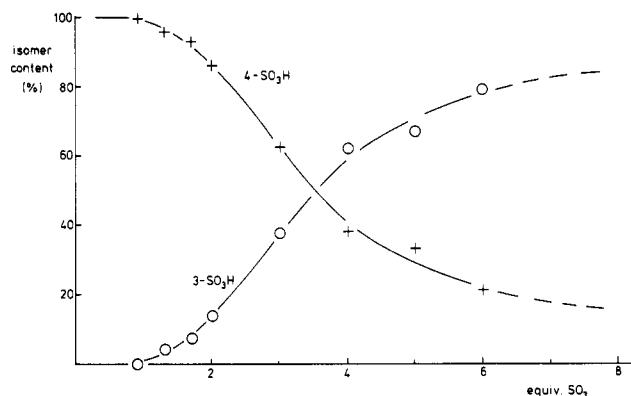


Figure 2. Sulfonation of 1 with SO<sub>3</sub> in nitromethane at 0 °C; dependence of sulfonate isomer distribution on the amount of SO<sub>3</sub> employed.

entries 1, 2, and 11-15) and of 4 (Figure 1) and 6 in nitromethane (Table II, entries 20-27 and 29-37, respectively). Accordingly, on using a deficient amount of SO<sub>3</sub> relative to the amount of phenol, the eventual conversion to the phenolsulfonic acid(s) will proceed by initial O-desulfonation of the phenyl hydrogen sulfate and subsequent C-sulfonation of the resulting phenol [steps -1 and 2], as observed for 6 (cf. Table II, entries 31-37). On the contrary, with an excess of SO<sub>3</sub> relative to the amount of phenol, the conversion of the phenyl hydrogen sulfate to the phenolsulfonic acid proceeds by C-sulfonation and subsequent O-desulfonation [steps 3, 4, and possibly 5],<sup>15</sup> as observed with 4 (Figure 1) and 6 (Table II, entries 21-27 and 30, respectively).

The regeneration of SO<sub>3</sub> from a phenyl hydrogen sulfate [step -1] is thought to proceed by an A-1 mechanism, as proposed by Kice for the hydrolysis of substituted sodium phenyl sulfates in weak aqueous mineral acids.<sup>16</sup> The observed independence of the rate constant for the conversion of phenyl hydrogen sulfate on the amount of phenol (Table III) is in agreement with the proposed A-1 mechanism. Intermolecular trans-sulfonation was observed also to occur on addition of 1,3-dimethoxybenzene, azulene, and 9-methylanthracene to phenyl hydrogen sulfate in nitromethane at 0 °C, the products being 1,3-dimethoxy-

(14) For the sulfonation in 90.4% H<sub>2</sub>SO<sub>4</sub> at 25 °C the reactivity ratio of phenyl methanesulfonate<sup>12</sup> (which is an ester homologue of phenyl hydrogen sulfate) and phenol<sup>12</sup> is  $(1.6 \times 10^{-6}) : (17000 \times 10^{-6}) = 0.9 \times 10^{-4}$ .

(15) The rate of O-desulfonation will be greater for HO<sub>3</sub>SR<sub>2</sub>C<sub>6</sub>H<sub>2</sub>OSO<sub>3</sub>H than for R<sub>2</sub>C<sub>6</sub>H<sub>3</sub>OSO<sub>3</sub>H in view of the electron-withdrawing effect of the C-bonded sulfo group.

(16) Kice, J. L.; Anderson, J. M. *J. Am. Chem. Soc.* 1966, 88, 5242.

Table V. Pseudo-First-Order-Sulfonation Rate Constants

| % H <sub>2</sub> SO <sub>4</sub> | 10 <sup>7</sup> k <sub>1</sub> , s <sup>-1</sup> (25 °C) |                 |                |                |                 |               |
|----------------------------------|--|-----------------|----------------|----------------|-----------------|---------------|
|                                  | 1  |                 |                | 5              |                 |               |
|                                  | overall  | 3- <sup>a</sup> | 4-             | overall        | 3- <sup>a</sup> | 4-            |
| 75.0                             | 30 ± 15  | 2.3 ± 1.2       | 25 ± 13        | 14 ± 7         | 4 ± 2           | 6 ± 3         |
| 80.0                             | 1150 ± 350   | 110 ± 35        | 930 ± 280      | 750 ± 120      | 260 ± 40        | 225 ± 40      |
| 84.5                             |  |                 |                |                |                 |               |
| 84.9                             | 43 000 ± 6 000   | 5 800 ± 900     | 31 000 ± 4 000 |                |                 |               |
| 89.1                             |  |                 |                | 7 000 ± 700    | 2 700 ± 280     | 1 540 ± 160   |
| 91.5                             |  |                 |                | 37 000 ± 5 000 | 14 600 ± 2 000  | 7 400 ± 1 000 |

<sup>a</sup>The data refer strictly to the 3-position only.

benzene-4-, azulene-1-, and 9-anthrylmethanesulfonic acids, respectively.<sup>17</sup>

The variation in the ratio of 3- to 4-substitution in the sulfonation of 2,6-dimethylphenol (1) with the SO<sub>3</sub> to substrate ratio (Figure 2) may be explained in terms of the occurrence of both the steps 2 and 3 as the predominant reactions. In view of the electron-withdrawing effect of the sulfo group the phenyl hydrogen sulfate will be far less reactive for ring sulfonation than the corresponding phenol. The 3- to 4-sulfonate isomer ratio, observed for a low content of SO<sub>3</sub> (viz., <0.02) is thus that of the phenol species proper. Upon increasing the content of SO<sub>3</sub> the relative concentration of the hydrogen sulfate increases at the expense of the phenol. The decrease in the degree of 4-substitution is therefore ascribed to a decrease in the sulfonation of the phenol and additional sulfonation of the phenyl hydrogen sulfate. The limiting 3- to 4-sulfonate isomer distribution for high SO<sub>3</sub> content, viz., 86:14 (cf. Figure 2), is considered to be the isomer distribution for sulfonation of the phenyl hydrogen sulfate. The lower reactivity of a phenyl hydrogen sulfate as compared to the corresponding phenol is due to the conjugative electron release of phenoxy oxygen to the SO<sub>3</sub>H group, thus reducing the positive mesomeric effect of that oxygen toward the phenyl group. For the 2,6-dimethyl derivative there will be an additional decrease in the conjugative electron release of the OSO<sub>3</sub>H oxygen to the phenyl group, since the OSO<sub>3</sub>H sulfo group is rotated out of the plane of the 2,6-dimethylphenyl moiety because of steric repulsion by the two adjacent methyls.

**Sulfonation in Sulfuric Acid.** The sulfonation of 2,6-dimethylanisole (5) in concentrated aqueous sulfuric acid leads to the formation of the 3- and 4-sulfonic acid, the ratio of which increases from 1.00 to 4.2 upon increasing the sulfuric acid concentration from 75% to 96%. Sulfonation of the corresponding phenol 1 leads to the formation of a mixture of the 3- and 4-sulfonic acids and their hydrogen sulfates. For a given sulfuric acid concentration the ArOSO<sub>3</sub>H:ArOH ratio is independent of the reaction time, as was also established for phenol-3- and -4-sulfonic acid.<sup>18</sup> Further, the same ArOSO<sub>3</sub>H:ArOH ratio is found upon dissolving the sulfonic acids in sulfuric acid. Accordingly, the rates of the steps of the sulfation equilibrium of the phenolsulfonic acids are rapid relative to the rate of ring sulfonation. The content of the hydrogen sulfate increases with increasing sulfuric acid concentration, as shown in Figure 3. The degree of sulfation is lower for the 4- than the 3-sulfonic acid. This may be explained in terms of conjugative electron release from the OH to the SO<sub>3</sub>H group in 2,6-dimethylphenol-4-sulfonic acid; this effect is virtually absent in the corresponding phenol-3-sulfonic acid. The 1,4-conjugative in-

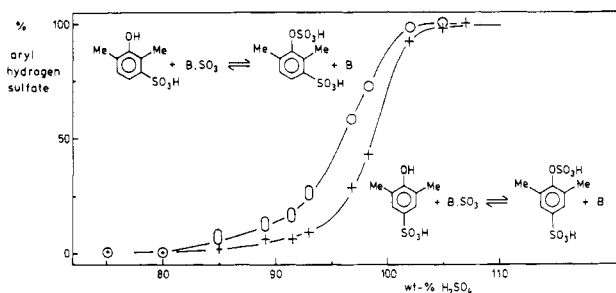


Figure 3. Content of aryl hydrogen sulfate of 2,6-dimethylphenol-3- (o) and -4-sulfonic acid (+).

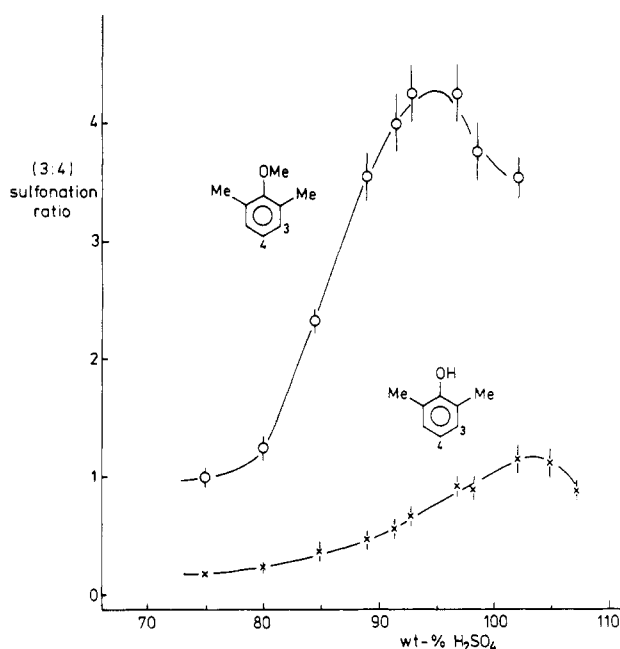


Figure 4. Ratio of 3- to 4-sulfonic acid in the sulfonation of the 2,6-dimethyl derivatives of phenol and anisole.

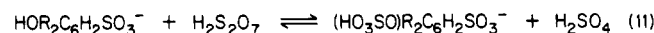
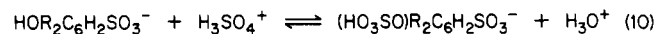
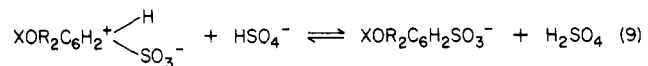
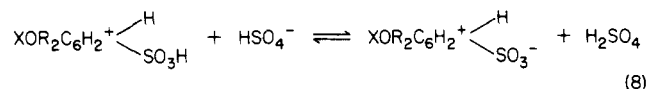
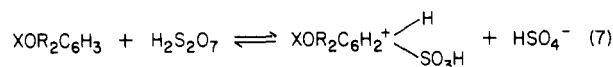
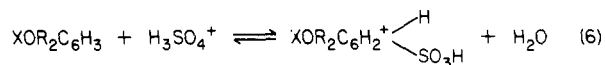
teraction will be far less in the 4-sulfophenyl hydrogen sulfate than in the corresponding phenol-4-sulfonic acid, as the OSO<sub>3</sub>H sulfo group is rotated out of the plane of the phenyl group as result of steric hindrance with the adjacent methyl groups.

It was established that the sulfonation of phenol and anisole in 74–90% H<sub>2</sub>SO<sub>4</sub> proceeds by substitution of the entity PhOX (X = H, Me), the protonated PhO<sup>+</sup>XH (X = H, Me) and the sulfated species PhOSO<sub>3</sub>H being far less reactive.<sup>12</sup> The sulfonation of 1 (X = H), 2 (X = *i*-Pr), and 5 (X = Me) will thus proceed by steps 6–9 in which the  $\sigma$ -complex-forming step (6) dominates at low sulfuric acid concentrations and step 7 dominates at high sulfuric acid concentrations,<sup>19,20</sup> these steps are rate limiting for sulfuric

(17) Goossens, H.; Lambrechts, H. J. A.; Cerfontain, H., unpublished results.

(18) Lambrechts, H. J. A.; Koeberg-Telder, A.; Cerfontain, H., unpublished results.

(19) Cerfontain, H.; Kort, C. W. F. *Int. J. Sulfur Chem. (C)*, 1971, 6, 123.



acid concentrations  $\leq 96\%$   $\text{H}_2\text{SO}_4$ .<sup>19</sup> The resulting phenolsulfonic acids are subsequently sulfated by steps 10 and 11, the former being the effective one at low and the latter at high sulfuric acid concentrations. The 3- to 4-sulfonation ratios of the unprotonated species of the phenols 1 and 2 and of the anisole 5, as determined from the sulfo product composition, are shown in Figure 4. The strong increase in the 3- to 4-sulfonation ratio with increasing sulfuric acid concentration observed with 1 and 5 is ascribed to the gradual changeover in the  $\sigma$ -complex-forming step from 6 to 7. There is a higher degree of sulfur-carbon bond formation and larger steric requirements with the former than the latter step,<sup>19</sup> as is apparent from the observed differences in the activation enthalpy and the activation entropy for the sulfonation of the 2- and 4-positions of toluene<sup>21</sup> and the 3- and 4-positions of *o*-xylene<sup>8</sup> by  $\text{H}_3\text{SO}_4^+$  and  $\text{H}_2\text{S}_2\text{O}_7$ . The increase in the degree of sulfonation at the 3-position of both 1 and 5 with increasing sulfuric acid concentration (cf. Figure 4) is therefore ascribed mainly to the lower degree of steric hindrance for the  $\text{H}_2\text{S}_2\text{O}_7$  as compared with the  $\text{H}_3\text{SO}_4^+$  type of sulfonation. The lower limit of the 3- to 4-sulfonation ratios, viz., 0.18 for 1 and 1.00 for 5 (cf. Figure 4), then are in fact the sulfonation ratios for the sulfonation by the  $\text{H}_3\text{SO}_4^+$  entity, and the maximal value of 4.26 for 5 at 92.9–96.9%  $\text{H}_2\text{SO}_4$  for its sulfonation by the entity  $\text{H}_2\text{S}_2\text{O}_7$ . The decrease in the 3- to 4-sulfonation ratio of 5 at acid concentrations  $>96.9\%$   $\text{H}_2\text{SO}_4$ <sup>22</sup> is ascribed to the fact that step 9 becomes rate limiting; it is very much more so for the formation of the sterically strained 3- than the 4-sulfonic acid as the  $\text{HSO}_4^-$  concentration decreases steeply from 90% to 100%  $\text{H}_2\text{SO}_4$ .<sup>24</sup> For the phenol 1, the same type of decrease would be expected for the sulfonation of the phenolic entity. Instead, the 3- to 4-sulfonation ratio continues to increase above 95%  $\text{H}_2\text{SO}_4$ . This is ascribed to additional sulfonation of the aryl hydrogen sulfate species.<sup>25</sup> As discussed in the previous sections, the hydrogen sulfate of 1 will lead to a higher

degree of 3-substitution than 1 itself.

In weak oleum up to 104%  $\text{H}_2\text{SO}_4$  the sulfonating entity is  $\text{H}_3\text{S}_2\text{O}_7^+$  and at higher acid concentration a polysulfuric acid, most probably  $\text{H}_2\text{S}_4\text{O}_{10}$ .<sup>19,27</sup> Apparently, the 3- to 4-sulfonation ratio of the hydrogen sulfate of 1 by the former is  $\sim 1.2$  and that of the latter  $\sim 0.9$ . The ratios of 3- to 4-sulfonation are far lower for the phenol 1 than the anisole 5. This is ascribed mainly to a lower degree of 4-substitution of 5, since its methoxy methyl will be rotated out of the plane of the phenyl group to a significantly higher degree than the hydroxy hydrogen of 1 in view of steric repulsion by the 2- and 6-methyls. Accordingly, the conjugative stabilization of the transition state leading to the  $\sigma$ -complex for 4-substitution will be less with 5 than 1.

For the sulfonation of phenol (6) in sulfuric acid up to an acid concentration of 85%  $\text{H}_2\text{SO}_4$  the rate of sulfonation is proportional to  $a_{\text{H}_3\text{SO}_4^+}$ , the plot of  $\log k_1$  vs.  $\log a_{\text{H}_3\text{SO}_4^+}$  being linear with a slope of 0.83,<sup>12</sup> indicating that the only effective  $\sigma$ -complex-forming step in that acid region is 6. At higher sulfuric acid concentrations there is an upward curvature in the plot,<sup>12</sup> indicating that there is additional sulfonation by  $\text{H}_2\text{S}_2\text{O}_7$ .<sup>19</sup> As to 1 and 5 the slopes of  $\log k_1$  vs.  $\log a_{\text{H}_3\text{SO}_4^+}$  for 4-substitution are both 1.00, indicating that the predominant initial step is 6. The slopes for 3-substitution of 1 and 5 (1.11 and 1.21, respectively) are higher than those for 4-substitution, illustrating that the gradual changeover from the  $\text{H}_3\text{SO}_4^+$  [steps 6, 8, and 9] to the  $\text{H}_2\text{S}_2\text{O}_7$  mechanism [steps 7–9], the steric requirements of which are less than that of the  $\text{H}_3\text{SO}_4^+$  mechanism, takes place at lower sulfuric acid concentration for the 3- than for the 4-sulfonation, the latter substitution being devoid of steric hindrance for both 1 and 5.<sup>28</sup> The slope is higher for the 3-position of 5 (1.21) than for that of 1 (1.11), indicating that the gradual changeover of the sulfonating entity from  $\text{H}_3\text{SO}_4^+$  to  $\text{H}_2\text{S}_2\text{O}_7$  occurs at a lower acid concentration for the 3-positions of 5 than 1. This is ascribed to a higher degree of buttressing of the 2-methyl group by the OR group for 5 ( $\text{R} = \text{Me}$ ) than 1 ( $\text{R} = \text{H}$ ).

**Steric Inhibition of OR ( $\text{R} = \text{H}, \text{Me}, \text{SO}_3\text{H}$ ) Conjugation.** The partial rate factor ratios for the sulfonation of the 2,6-disubstituted substrates,  $f_3/f_4$ , are collected in Table VI. With most of the substrates, the ortho substituents induce torsion around the C(1)–O bond for steric reasons. The torsion angles,  $\varphi$ , estimated from studies with Catalin Stuart molecular models for two conformations of the ortho alkyl groups, viz., those in which the  $\text{C}_\alpha$  hydrogen (or the  $\text{C}_\alpha$  methyl as with 3) is anti and eclipsed relative to C(1), are also given in Table VI. The conformation with the lower  $\varphi$  will be the higher populated one, as the reduction in conjugative stabilization between the oxygen and phenyl will be less than for the conformation with the higher  $\varphi$ . The  $f_3/f_4$  ratio of phenol (6), phenyl hydrogen sulfate (6-OSO<sub>3</sub>H), and anisole (7) for both  $\text{MeNO}_2\cdot\text{SO}_3$  and  $\text{H}_3\text{SO}_4^+$  as reagent is  $<0.01$ , illustrating the relatively strong mesomeric stabilization of the transition state leading to 4-substitution by the oxygen of the OR ( $\text{R} = \text{H}, \text{SO}_3\text{H}, \text{and Me}$ ) substituent which is in the plane of the phenyl group.

On the basis of the Hammett–Brown relation, assuming additivity of substituent effects, it can be derived that the

(20) Upon increasing the sulfuric acid concentration from 70% to 99%  $\text{H}_2\text{SO}_4$ , there is a gradual change in the sulfonating entity from  $\text{H}_3\text{SO}_4^+$  to  $\text{H}_2\text{S}_2\text{O}_7$ .<sup>19</sup>

(21) Cerfontain, H.; Sixma, F. L. J.; Vollbracht, L. *Recl. Trav. Chim. Pays-Bas* 1963, 82, 659.

(22) A similar decrease in the rate ratio at acid concentrations above 95%  $\text{H}_2\text{SO}_4$  was observed for the 2- and 4-sulfonation of toluene<sup>21,23</sup> and the 3- and 4-sulfonation of *o*-xylene.<sup>8</sup>

(23) Koeberg-Telder, A.; Cerfontain, H. *Recl. Trav. Chim. Pays-Bas* 1971, 90, 193.

(24) Cerfontain, H. "Mechanistic Aspects in Aromatic Sulfonation and Desulfonation"; Interscience Publishers: New York, 1968; pp 2–4.

(25) The degree of aryl hydrogen sulfate formation of 1 in sulfuric acid  $>95\%$   $\text{H}_2\text{SO}_4$  will be very high, as it will be greater than that of the 3- and 4-sulfonic acid of 1. It is known for both *p*-hydroxy- and *p*-methoxyphenol that the content of hydrogen sulfate decreases upon replacing a phenyl hydrogen by a sulfonic acid group.<sup>26</sup>

(26) Koeberg-Telder, A.; Lambrechts, H. J. A.; Cerfontain, H. *J. Chem. Soc., Perkin Trans. 2*, submitted for publication.

(27) Kort, C. W. F.; Cerfontain, H. *Recl. Trav. Chim. Pays-Bas* 1970, 88, 1298.

(28) For aromatic hydrocarbons, the sulfuric acid concentration of equal rate contributions by steps 6 and 7 is significantly lower for substituents that encounter steric hindrance. The difference in sulfuric acid concentration of 50/50 rate contributions for the 2- and 4-positions of toluene are 6.4%  $\text{H}_2\text{SO}_4$ , for the 3- and 4-positions of *o*-xylene 9.2%  $\text{H}_2\text{SO}_4$ , and the 2- and 5-positions of *m*-xylene 8%  $\text{H}_2\text{SO}_4$ .<sup>19</sup>

Table VI. Ratios of Partial Rate Factors for 3- and 4-Sulfonation and Torsion Angles around C(1)-O

| no.                               | $f_3/f_4$                                   |   |  | conformational approach                    |                                   |
|-----------------------------------|---|---|--|--|-----------------------------------|
|                                   | MeNO <sub>2</sub> SO <sub>3</sub> ,<br>0 °C | H <sub>3</sub> SO <sub>4</sub> <sup>+</sup> (75%<br>H <sub>2</sub> SO <sub>4</sub> ), 25 °C | H <sub>2</sub> S <sub>2</sub> O <sub>7</sub> (95%<br>H <sub>2</sub> SO <sub>4</sub> ), 25 °C | H <sub>α</sub><br>orientation <sup>j</sup> | φ, <sup>a</sup><br>deg            |
| 1                                 | <0.01                                       | 0.088   | 0.40   | anti<br>eclipsed                           | 0 <sup>b</sup><br>40              |
| 1-OSO <sub>3</sub> H <sup>c</sup> | 3.9   |   |  | anti<br>eclipsed                           | 63<br>63                          |
| 2                                 | <0.005                                      |   | 0.015  | anti<br>eclipsed                           | 0 <sup>d</sup><br>40              |
| 2-OSO <sub>3</sub> H              | <0.01                                       |   |  | anti<br>eclipsed                           | 90 <sup>e</sup><br>63             |
| 3                                 | <0.005                                      |   |  | anti <sup>f</sup><br>eclipsed <sup>f</sup> | 0 <sup>d</sup><br>90 <sup>e</sup> |
| 4                                 | <0.01                                       |   |  |  | 0                                 |
| 4-OSO <sub>3</sub> H              | <0.01                                       |   |  |  | 58                                |
| 5                                 | 0.016                                       | 0.49  | 2.1  | anti<br>eclipsed<br>h                      | 55<br>60<br>41 <sup>h</sup>       |
| 6                                 | <0.01                                       | <0.01 <sup>i</sup>  |  |  | 0                                 |
| 6-OSO <sub>3</sub> H              | <0.01                                       | <0.01   |  |  | 27                                |
| 7                                 | <0.01                                       | <0.01 <sup>i</sup>  |  |  | 0                                 |

<sup>a</sup>Torsion angles estimated from Catalin Stuart Molecular models. <sup>b</sup>φ calculated from eq 12: H<sub>3</sub>SO<sub>4</sub><sup>+</sup>, ≤20°; H<sub>2</sub>S<sub>2</sub>O<sub>7</sub>, 24 ± 8. <sup>c</sup> $f_3/f_4$  for H<sub>3</sub>S<sub>2</sub>O<sub>7</sub><sup>+</sup> (102% H<sub>2</sub>SO<sub>4</sub>, 25 °C), 0.6; for H<sub>2</sub>S<sub>4</sub>O<sub>10</sub> (107% H<sub>2</sub>SO<sub>4</sub>, 25 °C), 0.45. <sup>d</sup>The hydroxy hydrogen is locked between the two adjacent methyls, rendering this conformer very unlikely. <sup>e</sup>This conformation is highly strained. <sup>f</sup>Orientation of Me<sub>α</sub> relative to C(1). <sup>g</sup>φ calculated from eq 12: H<sub>3</sub>SO<sub>4</sub><sup>+</sup>, 30 ± 6; H<sub>2</sub>S<sub>2</sub>O<sub>7</sub>, 43 ± 6. <sup>h</sup>Conformer for which φ is minimal. <sup>i</sup>Reference 12. <sup>j</sup>This is the H<sub>α</sub> orientation to C(1) using the C<sub>α</sub>-C(2) bond as the axis.

$f_3/f_4$  ratio for the substitution of 1, its hydrogen sulfate, and 5 is determined by step 12 in which  $\rho^+$  is the reaction

log  $f_3/f_4 =$

$$\rho^+[\sigma^+_{m-OR} + \sigma^+_{p-Me} + \sigma^+_{o-Me} - \sigma^+_{p-OR} \cos^2 \varphi - 2\sigma^+_{m-Me}] \quad (12)$$

constant,  $\sigma^+$  the substituent constant,  $\varphi$  the torsion angle of the OR group around the C(1)-O bond, and R is H, Me, or SO<sub>3</sub>H. For sulfonation with H<sub>3</sub>SO<sub>4</sub><sup>+</sup> and H<sub>2</sub>S<sub>2</sub>O<sub>7</sub> as reagent the  $\rho^+$  values are  $-9.3 \pm 0.3^{12}$  and  $-5.7 \pm 0.3^{19}$  respectively, but for the other listed reagents no  $\rho^+$  data are available. As to the MeNO<sub>2</sub>SO<sub>3</sub> reagent the sharp increase in  $f_3/f_4$  on going from 1 (<0.01) to its hydrogen sulfate ( $3.9 \pm 0.9$ ) is clearly due to reduction in the rate of 4-sulfonation, which is a result of the lower conjugative stabilization of the transition state by the C(1) bonded oxygen, due to the high torsion angle and the competing conjugative electron release from the phenoxy oxygen to its SO<sub>3</sub>H group. The strong reduction in  $f_3/f_4$  on going from 1-OSO<sub>3</sub>H ( $3.9 \pm 0.9$ ) to 2-OSO<sub>3</sub>H (<0.01) is due to steric hindrance by the two C<sub>α</sub> methyls which prevent the 3-position from being sulfonated.<sup>29</sup> The absence of 3-substitution with 3 is due to steric hindrance by the *tert*-butyl group at C(2). The very low  $f_3/f_4$  ratio for the sulfonation of 4 is thought to originate in the low rate of 3-substitution as result of deactivation by the chlorines, the  $\sigma^+$  values of *p*- (0.11<sup>6</sup>) and *o*-Cl (0.33<sup>7</sup>) being much greater than those of *p*- (-0.28<sup>6</sup>) and *o*-Me (-0.19<sup>7</sup>). For 5 the  $f_3/f_4$  ratio is only 0.016. This is only explainable if the actual  $\varphi$  is smaller than those of the anti and eclipsed conformation.<sup>30</sup> In fact, it appears from the molecular model that the minimal attainable  $\varphi$  is 41°. Upon using this value the form between brackets of 12 becomes positive (0.18), so that  $f_3/f_4 < 1$ .

Let us now consider the sulfuric acid sulfonations. It was emphasized by Taylor that the  $\sigma^+_{p-OMe}$  is substantially

greater in trifluoroacetic acid as solvent (-0.60<sup>31</sup>) than in a nonacidic solvent (-0.78<sup>6</sup>), as a result of hydrogen-bonding interactions by the former solvent.<sup>32</sup> The effective  $\sigma^+_{p-OMe}$  and  $\sigma^+_{p-OH}$  for concentrated aqueous sulfuric acid, estimated from the linear graph of log  $f$  vs.  $\sigma^+$  for sulfonation by H<sub>3</sub>SO<sub>4</sub><sup>+</sup><sup>12</sup> are both -0.42. Further  $\sigma^+_{m-OH}$  was assumed to be 0.05 [cf. ref 6]. The torsion angles of 5, calculated with equation 12, agree within experimental error with that of the conformer of lowest energy, estimated from the molecular model. The angles calculated for 1 are somewhat greater than zero, the torsion angle of the isolated molecule. This is ascribed to hydrogen bonding of the phenol oxygen by the acidic species present in sulfuric acid, a result of which is some torsion around the C(1)-O bond.

### Experimental Section

The substrates were obtained commercially. The <sup>1</sup>H NMR spectra were recorded on a Varian XL-100 spectrometer.

**Sulfonation Procedures and Analysis. A.** A solution of the phenols 1 (0.50 mmol) or 2 (0.34 mmol) in dioxane-*d*<sub>8</sub> (0.50 mL) was added to a solution of the desired amount of SO<sub>3</sub> in dioxane-*d*<sub>8</sub> (0.50 mL) at 17 °C. <sup>1</sup>H NMR spectra were recorded after appropriate time intervals.

**B.** To a solution of the phenols 1 or 4 (0.50 mmol) in nitromethane-*d*<sub>3</sub> (0.50 mL) was added at -30 °C a solution of the desired amount of SO<sub>3</sub> in nitromethane-*d*<sub>3</sub> (0.50 mL) and an <sup>1</sup>H NMR spectrum recorded. For the experiments with 4, the reaction temperature was subsequently raised at 60 °C and <sup>1</sup>H NMR spectra were recorded.

**C.** To a solution of phenol (6) (0.50 mmol) in nitromethane-*d*<sub>3</sub> (0.50 mL) was added at -35 °C under a nitrogen atmosphere the desired amount of SO<sub>3</sub> in nitromethane-*d*<sub>3</sub> (0.50 mL) and the reaction mixture left at -35 °C for 15 min. The temperature was raised to 0 °C and <sup>1</sup>H NMR spectra were recorded after appropriate time intervals. The conversion of phenyl hydrogen sulfate at 0 °C into phenol-4-sulfonic acid proceeds by first-order kinetics, the plots of log [PhOSO<sub>3</sub>H] vs. reaction time being linear up to 70% conversion.

**D.** To a solution of the substrate (1.00 mmol) in nitromethane (7.0 mL) was added at 0 °C a solution of the desired amount of

(29) As to the sulfonation of the 3-position, the steric situation in the C<sub>α</sub>H-C eclipsed conformation of 2-OSO<sub>3</sub>H is similar to that of the 3-position in 2,6-di-*tert*-butylphenol (3), which in fact is not sulfonated (see Table VII) for steric reasons.<sup>11</sup>

(30) Upon choosing the  $\varphi$  of 5 to be 55°, the form between brackets of equation 12 becomes negative (-0.02) and  $f_3/f_4$  necessarily >1.

(31) Baker, R.; Eaborn, C.; Taylor, R. *J. Chem. Soc., Perkin Trans.* 2, 1972, 97.

(32) Peterson, P. E. *J. Org. Chem.* 1966, 31, 439.

SO<sub>3</sub> in nitromethane (7.0 mL). After 30 min 1.0 mL of D<sub>2</sub>O was added and the mixture heated for 20 min at 60 °C to hydrolyze most of the sulfate and any anhydride. The aqueous layer was isolated and extracted at room temperature three times with CH<sub>2</sub>Cl<sub>2</sub> (1-2 mL) to remove any unreacted substrate and remaining solvent. Residual CH<sub>2</sub>Cl<sub>2</sub> was removed by bubbling N<sub>2</sub> through the aqueous solution for 30 min. Then for the product analysis an <sup>1</sup>H NMR spectrum was recorded. In some cases the D<sub>2</sub>O solution of the sulfonic acids was neutralized with dilute aqueous potassium hydroxide, the solvents were removed by freeze drying, and an <sup>1</sup>H NMR spectrum was recorded of the remaining mixture of potassium sulfonates in D<sub>2</sub>O.

E. The sulfonation of 1, 2, and 5 (0.50 M) in sulfuric acid of the desired strength was followed by recording <sup>1</sup>H NMR spectra of the homogeneous sulfuric acid solutions after appropriate time intervals. The solubility of 2 and its sulfonic acids was too low

to study the sulfonation of 2 at acid concentrations lower than 98% H<sub>2</sub>SO<sub>4</sub>. The composition of the reaction mixtures was determined by multicomponent <sup>1</sup>H NMR analysis.<sup>13</sup> The conversion of 1 and 5 was first order in the substrate, the plots of log [ArH] vs. time being linear up to at least 50% conversion.

**Acknowledgment.** The authors thank H. D. Goossens for assistance and Dr. K. Laali for a gift of 2,6-diisopropylphenol.

**Registry No.** 1, 576-26-1; 1-OSO<sub>3</sub>H, 92545-08-9; 2, 2078-54-8; 2-OSO<sub>3</sub>H, 92545-09-0; 3, 128-39-2; 4, 87-65-0; 4-OSO<sub>3</sub>H, 92545-10-3; 5, 1004-66-6; 6, 108-95-2; 6-OSO<sub>3</sub>H, 937-34-8; 7, 100-66-3.

**Supplementary Material Available:** Table I listing the <sup>1</sup>H NMR parameters of 1-6 and their sulfo derivatives (3 pages). Ordering information is given on any current masthead page.

## Photochemical Transformations and Laser Flash Photolysis Studies of Dibenzobarrelenes Containing 1,2-Dibenzoylalkene Moieties<sup>1</sup>

Challa V. Kumar,<sup>2a,b</sup> Bulusu A. R. C. Murty,<sup>2a</sup> Saswati Lahiri,<sup>2a</sup> Elizabeth Chackachery,<sup>2a</sup> Juan C. Scaiano,<sup>\*2b,c</sup> and Manapurathu V. George<sup>\*2a,b</sup>

Department of Chemistry, Indian Institute of Technology, Kanpur 208016, India, Radiation Laboratory and Department of Chemistry, University of Notre Dame, Notre Dame, Indiana 46556, and Division of Chemistry, National Research Council, Ottawa, Ontario, K1A 0R6 Canada

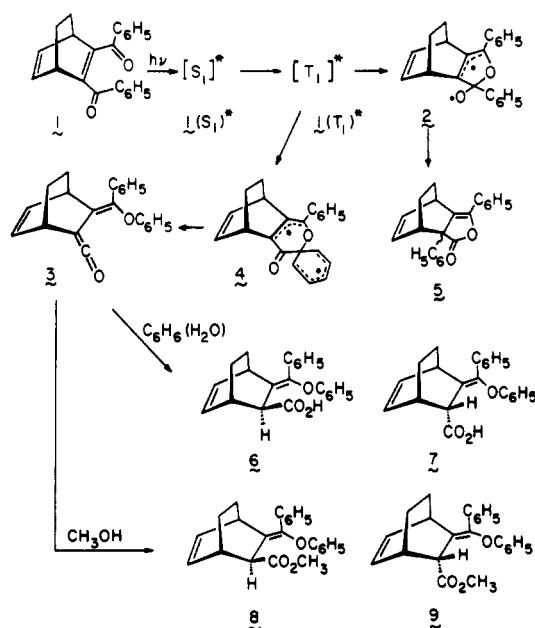
Received April 24, 1984

Phototransformations of the dibenzobarrelenes 10, 11, and 23, prepared by the reaction of the appropriate anthracenes with dibenzoylacetylenes, are reported. Irradiation of 10 and 11 in solvents such as benzene, methanol, and acetone gave the corresponding dibenzosemibullvalenes, 17 and 18, respectively, in good yields. These dibenzosemibullvalenes on catalytic hydrogenation using 5% Pd on charcoal gave the corresponding cyclopropane ring-opened products, 21 and 22, respectively. Irradiation of 23 in benzene gave a mixture of 2,3-dibenzoyl-2,3-dihydro-1,4-dimethyl-2,3-benzonaphthalene (27, 12%), 1,4-dibenzoyl-5,8-dimethyl-2,3,6,7-dibenzocyclooctatetraene (24, 20%), the carbinol 29 (45%), and benzoic acid (7%). Irradiation of 23 in methanol gave a mixture of 27 (25%), 24 (27%), and benzoic acid (8%). Laser flash photolysis (337.1 nm) of 10, 11, and 23 led to transient species, characterized by strong absorptions in the 300-650-nm region. These transients are due to the triplet states of the substrates, as established by quenching studies involving oxygen, di-*tert*-butylnitroxide, azulene, and β-carotene. Energy-transfer sensitization of 10, 11, and 23 by benzophenone in benzene also gave rise to the same transients, as formed under direct irradiation. The quantum yields of triplet formation (Φ<sub>T</sub>) were estimated to be high for 10 and 11 (~1), whereas it is significantly lower for 23 (~0.7).

### Introduction

It has been reported earlier that dibenzoylethylenes undergo an interesting photorearrangement in protic solvents such as alcohols, besides *cis*-*trans* isomerization, which results in the corresponding butenoic esters.<sup>3-7</sup> Recent studies have shown that *cis*-1,2-dibenzoylalkenes, having rigid structural features and wherein the *cis*-*trans* isomerization is prevented, undergo the photorearrangement predominantly.<sup>8</sup> Thus, the photolysis of 2,3-dibenzoylbicyclo[2.2.2]octa-2,5-diene (1), for example, gave a mixture of 6-(1-phenoxy-1-phenylmethylene)bicyclo[2.2.2]oct-2-ene-5-*exo*-carboxylic acid (6), 6-(1-phenoxy-1-phenylmethylene)bicyclo[2.2.2]oct-2-ene-5-*endo*-

Scheme I



(1) Document No. NDRL-2579 from the Notre Dame Radiation Laboratory.

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carboxylic acid (7), and the lactone 5, whereas irradiation of 1 in methanol gave a mixture of methyl 6-(1-phenoxy-1-phenylmethylene)bicyclo[2.2.2]oct-2-ene-5-*exo*-