

## Aromatic Sulphonation. Part 74.<sup>1</sup> Sulphonation of Some 9-Alkenyl-anthracenes and the Corresponding Benzenes with Dioxan-SO<sub>3</sub>

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The sulphonation of six alkenylarenes with dioxan-SO<sub>3</sub> in dioxan has been studied at 17 °C. With the substrates 9-vinyl- (3a), 9-(prop-2-enyl)- (3b), and 9-[(*E*)-but-2-enyl]-anthracene (3c), and (*E*)-prop-1- and -2-enylbenzene (3d and e) unsaturated pyrosulphonic acids are obtained with the double bond at C- $\alpha$  and the pyrosulphonic acid group at C- $\beta$ - for the substrates (3a, b, d, and e), and the double bond at C- $\beta$  and the pyrosulphonic acid group at C- $\gamma$  for (1c). The prop-2-enyl derivatives (3b and e) yielded, besides a minor quantity of the above mentioned pyrosulphonic acids, mainly 2-arylprop-1-ene-3-sulphonic acids, and substrate (3d) the *cis*- and *trans*-isomer of the cyclic sulphonate sulphate anhydride (5d). All these sulpho-products result from direct attack of SO<sub>3</sub> on the side-chain double bond. 9-[(*E*)-prop-1-enyl]anthracene yields sodium (*E*)-1-(9-anthryl)prop-1-ene-3-sulphonate as the main product. It is suggested that this product results from initial attack of SO<sub>3</sub> at the 10-position of the anthryl group followed by the reaction sequence proposed in the preceding paper. The behaviour of the presently investigated anthracene derivatives is compared with the behaviour of both the corresponding saturated anthracene analogues and the corresponding side-chain benzene analogues.

RECENTLY we reported on the behaviour of some 9-alkylanthracenes towards dioxan-SO<sub>3</sub> as sulphonating medium.<sup>1,2</sup> The formation of the products was explained in terms of the initial formation of the corresponding 9-(alk-1-enyl)anthracenes in a redox reaction, which intermediates were then rapidly sulphonated. In some cases, depending on the structure of the alkyl group, this intermediate could be detected in the reaction mixture by <sup>1</sup>H n.m.r. It was thought of interest to study the sulphonation of some of these intermediates and to compare their behaviour with that of the corresponding benzenes.

### RESULTS

The reactions of 9-vinyl-, 9-[(*E*)-but-2-enyl]-, † 9-[(*E*)-prop-1-enyl]-, and 9-(prop-2-enyl)-anthracene and those of the corresponding benzene derivatives of the last two compounds, *viz.* (*E*)-prop-1- and -2-enylbenzene, with *ca.* 1 equiv. [<sup>2</sup>H<sub>8</sub>]dioxan-SO<sub>3</sub> complex in [<sup>2</sup>H<sub>8</sub>]dioxan have been investigated at 17 °C. The composition of the reaction mixtures was determined both during and after the reaction by <sup>1</sup>H n.m.r. multicomponent analysis.<sup>3</sup> ‡ The <sup>1</sup>H n.m.r. data of the investigated substrates and the products are listed in Tables 1 and 2, respectively.

In the reaction mixtures of 9-vinyl- and 9-[(*E*)-prop-1-enyl]anthracene with dioxan-SO<sub>3</sub> considerable amounts, in those of 9-(prop-2-enyl)- and 9-[(*E*)-but-2-enyl]-anthracene and (*E*)-prop-1-enylbenzene only small amounts, of un-

† The (*E*)-configuration is based on the use of (*E*)-1-chlorobut-2-ene and (*E*)-1-bromoprop-1-ene respectively as starting compound in the synthesis of these substrates. With 9-[(*E*)-prop-1-enyl]anthracene this assignment is supported by the observable vinyl coupling with *J* 16 Hz.

‡ In the reactions with [<sup>2</sup>H<sub>8</sub>]dioxan-SO<sub>3</sub> complex in [<sup>1</sup>H<sub>8</sub>]dioxan no dioxan decomposition products<sup>4</sup> were formed.

§ The differences in the chemical shifts between hydrogens attached to a carbon which carries a sulphonic or a pyrosulphonic acid group are only small, *e.g.* the methyl hydrogens of MeS<sub>2</sub>O<sub>6</sub>H are 21 Hz to lower field than those of MeSO<sub>3</sub>H.<sup>5</sup> So, from the observed chemical shifts for the hydrogens under discussion no distinction can be made between a sulphonic and pyrosulphonic acid group. The requirement of *ca.* 2 equiv. of SO<sub>3</sub> indicates the formation of the pyrosulphonic acid, and its formation is further supported by mechanistic reasons (see Discussion section).

known (probably polymeric) products were present. These types of products are absent in the reaction of prop-2-enylbenzene with dioxan-SO<sub>3</sub>.

9-Vinylanthracene.—The reaction of 9-vinylanthracene yielded as detectable product (*E*)-(9-anthryl)ethylenepyrosulphonic acid.§|| The assignment of this pyrosulphonic acid was based mainly on the positions of the two vinylic hydrogens and on double-resonance experiments with these hydrogens. The (*E*)-configuration is based on the observable vinyl coupling with *J* 16 Hz.

9-[(*E*)-Prop-1-enyl]anthracene.—The reaction of 9-[(*E*)-prop-1-enyl]anthracene with dioxan-SO<sub>3</sub> has been carried out at a lower substrate concentration than that of the other substrates (0.04 instead of 0.8M) to reduce dimer and polymer formation. The main isolated product is sodium (*E*)-1-(9-anthryl)prop-1-ene-3-sulphonate (vinylic *J* 16 Hz).

9-(Prop-2-enyl)anthracene.—The reaction of 9-(prop-2-enyl)anthracene yielded 5 ± 2% unconverted substrate, 86 ± 4% 2-(9-anthryl)prop-1-ene-3-sulphonic acid (6b) (see Scheme 1)¶ and 9 ± 2% 2-(9-anthryl)prop-1-ene-1-pyrosulphonic acid (4b).\*\*

9-[(*E*)-But-2-enyl]anthracene.—In the reaction of 9-[(*E*)-but-2-enyl]anthracene (38 ± 3% unconverted substrate) two pyrosulphonic acids have been obtained, *viz.* (*E*)- and (*Z*)-1-(9-anthryl)but-2-ene-3-pyrosulphonic acid in yields of 14 ± 2 and 48 ± 3%, respectively.

(*E*)-Prop-1-enylbenzene.—The sulphonation mixture of (*E*)-prop-1-enylbenzene consisted of 40 ± 3% unconverted substrate, 48 ± 3% of the *trans*-isomer of the cyclic sulphonate sulphate anhydride (5d) (see Scheme 1), the *trans* assignment of which is based on the doublet (*J* 11 Hz) at

|| The same product, but much less contaminated, has been obtained on reaction of 1-(9-anthryl)-1-hydroxyethane with dioxan-SO<sub>3</sub>. It is likely that initially 9-vinylanthracene is formed by dehydration of this substrate. Apparently 9-vinylanthracene is then sulphonated rapidly relative to its rate of formation thus rendering its concentration low, and this will accordingly lead to a lower degree of polymer formation than upon starting with 9-vinylanthracene proper.

¶ The assignment of (6b) containing a sulphonic acid group is based on the use of 1 equiv. SO<sub>3</sub>.

\*\* The configuration at the double bond could not be established in the absence of a vinylic coupling. It is thought to be *E* in view of the similarity in the chemical shifts of the  $\beta$ -hydrogens of (2a and b) (see Table 2).

TABLE 1  
<sup>1</sup>H N.m.r. data of the alkenylarenes in [<sup>2</sup>H<sub>8</sub>]dioxan

| Com-<br>pound     | δ                       |                  |                   |                                  |                  |                  |
|-------------------|-------------------------|------------------|-------------------|----------------------------------|------------------|------------------|
|                   | 1- and 8-H <sup>a</sup> | α-H <sup>b</sup> | α'-H <sup>b</sup> | β-H <sup>b</sup>                 | γ-H <sup>b</sup> | δ-H <sup>b</sup> |
| (3a)              | 8.42 (m)                | ca. 7.6 (1 H, m) |                   | 5.73 (1 H, dd)<br>6.07 (1 H, dd) |                  |                  |
| (3b)              | 8.27 (m)                |                  | 2.37 (3 H, s)     | 5.27 (1 H, s)<br>5.89 (1 H, s)   |                  |                  |
| (3c)              | 8.58 (m)                | 5.32 (2 H, m)    |                   | 6.58 (1 H, m)                    | 5.16 (1 H, m)    | 1.85 (3 H, d)    |
| (3d) <sup>e</sup> |                         | 6.39 (1 H, m)    |                   | 6.51 (1 H, m)                    | 2.01 (3 H, d)    |                  |
| (3c) <sup>e</sup> |                         |                  | 2.32 (3 H, s)     | 5.27 (1 H, s)<br>5.67 (1 H, s)   |                  |                  |
| (8)               | 8.30 (m)                | 7.20 (1 H, d)    |                   | 6.45 (1 H, dq)                   | 1.55 (3 H, dd)   |                  |

<sup>a</sup> 2-, 3-, 6-, and 7-H of the 9-alkenylantracenes give a multiplet of a total width of 15 Hz centred at δ 7.60 ± 0.05, and 4- and 5-H a multiplet of 15 Hz width centred at δ 8.14 ± 0.05. 10-H exhibits a singlet which for the hydrocarbons is at δ 8.51 ± 0.04, but for the sulphonated products (see Table 2) is at 8.60 ± 0.02. <sup>b</sup> α, β, etc. refers to the carbon of the side-chain. In the prop-2-enyl derivatives α-C represents the *sp*<sup>3</sup> carbon, and β-C the terminal carbon of the double bond. <sup>c</sup> The aromatic hydrogens exhibit a multiplet at δ 7.3–7.9.

TABLE 2  
<sup>1</sup>H N.m.r. data of the sulphonated products

| Product            | Solvent   | δ                       |                  |                   |                                |                  |                  |
|--------------------|---|-------------------------|------------------|-------------------|--------------------------------|------------------|------------------|
|                    |   | 1- and 8-H <sup>a</sup> | α-H <sup>b</sup> | α'-H <sup>b</sup> | β-H <sup>b</sup>               | γ-H <sup>b</sup> | δ-H <sup>b</sup> |
| (4a)               | [ <sup>2</sup> H <sub>8</sub> ]Dioxan             | 8.37 (m)                | 8.61 (1 H, d)    |                   | 7.26 (1 H, d)                  |                  |                  |
| (4b) <sup>c</sup>  | [ <sup>2</sup> H <sub>8</sub> ]Dioxan             |                         |                  | 2.81 (3 H, s)     | 6.90 (1 H, s)                  |                  |                  |
| (4b)               | [ <sup>2</sup> H <sub>8</sub> ]Dioxan             | 8.39 (m)                |                  |                   | 5.78 (1 H, s)<br>6.50 (1 H, s) | 4.59 (2 H, s)    |                  |
| (E)-(4c)           | [ <sup>2</sup> H <sub>8</sub> ]Dioxan             | 8.20 (m)                | 3.60 (2 H, d)    |                   | 6.50 (1 H, t)                  |                  | 2.40 (3 H, s)    |
| (Z)-(4c)           | [ <sup>2</sup> H <sub>8</sub> ]Dioxan             | 8.20 (m)                | 4.50 (2 H, d)    |                   | 5.90 (1 H, t)                  |                  | 2.40 (3 H, s)    |
| (4d)               | [ <sup>2</sup> H <sub>8</sub> ]Dioxan             | <i>d</i>                | 6.84 (1 H, s)    |                   | 2.45 (3 H, s)                  |                  |                  |
| <i>cis</i> -(5d)   | [ <sup>2</sup> H <sub>8</sub> ]Dioxan             | <i>d</i>                | 6.08 (1 H, d)    |                   | 4.59 (1 H, dq)                 | 1.46 (3 H, d)    |                  |
| <i>trans</i> -(5d) | [ <sup>2</sup> H <sub>8</sub> ]Dioxan             | <i>d</i>                | 6.80 (1 H, d)    |                   | ca. 4.6 (m)                    | 1.53 (3 H, d)    |                  |
| (4e)               | [ <sup>2</sup> H <sub>8</sub> ]Dioxan             | <i>d</i>                |                  | 2.70 (3 H, s)     | 6.96 (1 H, s)                  |                  |                  |
| (6e)               | [ <sup>2</sup> H <sub>8</sub> ]Dioxan             | <i>d</i>                |                  | 4.54 (2 H, s)     | 5.76 (1 H, s)                  |                  |                  |
| (7e)               | [ <sup>2</sup> H <sub>8</sub> ]Dioxan             | <i>d</i>                |                  | 5.36 (2 H, s)     | 6.01 (1 H, s)                  |                  |                  |
| (9) <sup>e</sup>   | [ <sup>2</sup> H <sub>8</sub> ]Dioxan             | 8.48 (m)                | ca. 7.6 (1 H, d) |                   | 7.14 (1 H, s)                  | 4.46 (2 H, d)    |                  |
| (1) <sup>f</sup>   | [ <sup>2</sup> H <sub>8</sub> ]Dimethyl sulfoxide | <i>d</i>                | 6.35 (1 H, m)    |                   | 6.26 (1 H, dt)                 |                  |                  |
| (2a)               | [ <sup>2</sup> H <sub>6</sub> ]Dimethyl sulfoxide | <i>d</i>                | 5.41 (1 H, d)    |                   | 3.55 (2 H, m)                  |                  |                  |
| (2b)               | [ <sup>2</sup> H <sub>6</sub> ]Dimethyl sulfoxide | <i>d</i>                | 5.92 (1 H, d)    |                   | 2.88 (1 H, dq)                 | 1.03 (3 H, d)    |                  |
| (2c)               | [ <sup>2</sup> H <sub>6</sub> ]Dimethyl sulfoxide | <i>d</i>                | 4.65 (1 H, d)    |                   | 2.8 (1 H, m)                   | 1.15 (3 H, d)    |                  |
|                    |   |                         |                  |                   | 2.8 (1 H, m)                   | 0.84 (3 H, d)    |                  |

<sup>a, b</sup> As Table 1. <sup>c</sup> Only the positively assigned absorptions are listed. <sup>d</sup> See footnote *c* of Table 1. <sup>e</sup> These are in fact the values of (9) formed in the reaction of 9-propylantracene with dioxan-SO<sub>3</sub> in dioxan,<sup>2</sup> as it appeared that the absorptions of (9) in the spectra of the sulphonates obtained on reaction of (8) and 9-propylantracene are identical. <sup>f</sup> Data from ref. 6.

δ 6.13 for the α-hydrogen,\* 10 ± 2% of the *cis*-isomer, based on the doublet (*J* 1.5 Hz) at δ 6.76 for the α-hydrogen,\* and ca. 2% of 1-phenylprop-1-ene-2-pyrosulphonic acid as detectable products.† The signals of the anhydrides (5d) disappeared after 6 h.

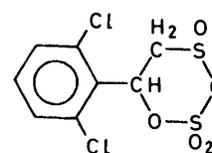
The assignment of the anhydride structure (5d) is based on the following evidence. First, sulphonation with 1 equiv. SO<sub>3</sub> gives substrate conversion and product formation both of ca. 50%, illustrating that 2 mol of SO<sub>3</sub> are required per mol of substrate. Secondly the positions and multiplicities of the <sup>1</sup>H n.m.r. signals of the products obtained (see Table 2) and their agreement with those of the cyclic sulphonate sulphate anhydride (1) obtained from 2,6-dichlorophenylethylene (see Table 2).<sup>7</sup>

Finally on pouring the mixture into ice-water followed by neutralization with NaOH the anhydrides should be hydro-

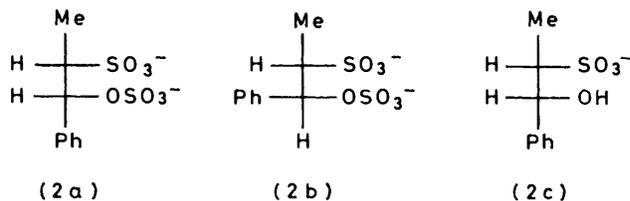
\* On the assumption that the anhydride (5) has a chair structure similar to that of cyclohexane it follows that the α- and β-side-chain carbons and their hydrogens in the *trans*-isomer are approximately in one plane, whereas for the *cis*-isomer they are not. Using the Karplus equation it then follows that the coupling constant between the vicinal α- and β-hydrogens is greater with the *trans*-than with the *cis*-isomer.

† Anhydrides (5) were also detected as intermediates in the reaction of 3-phenylpropan-1-ol with concentrated H<sub>2</sub>SO<sub>4</sub>, eventually leading to 1-(*p*-sulphophenyl)prop-1-ene-2-sulphonic acid as the main product.<sup>6</sup>

lysed<sup>8</sup> as is in fact observed. The three products resulting are tentatively assigned as the two possible disodium salts of the sulphate of 1-phenyl-1-hydroxypropane-3-sulphonate,



(1)



*viz.* 65% (2a) and 15% (2b), and the sodium salt of 1-phenyl-1-hydroxypropane-2-sulphonate (20%) (2c).‡ Pre-

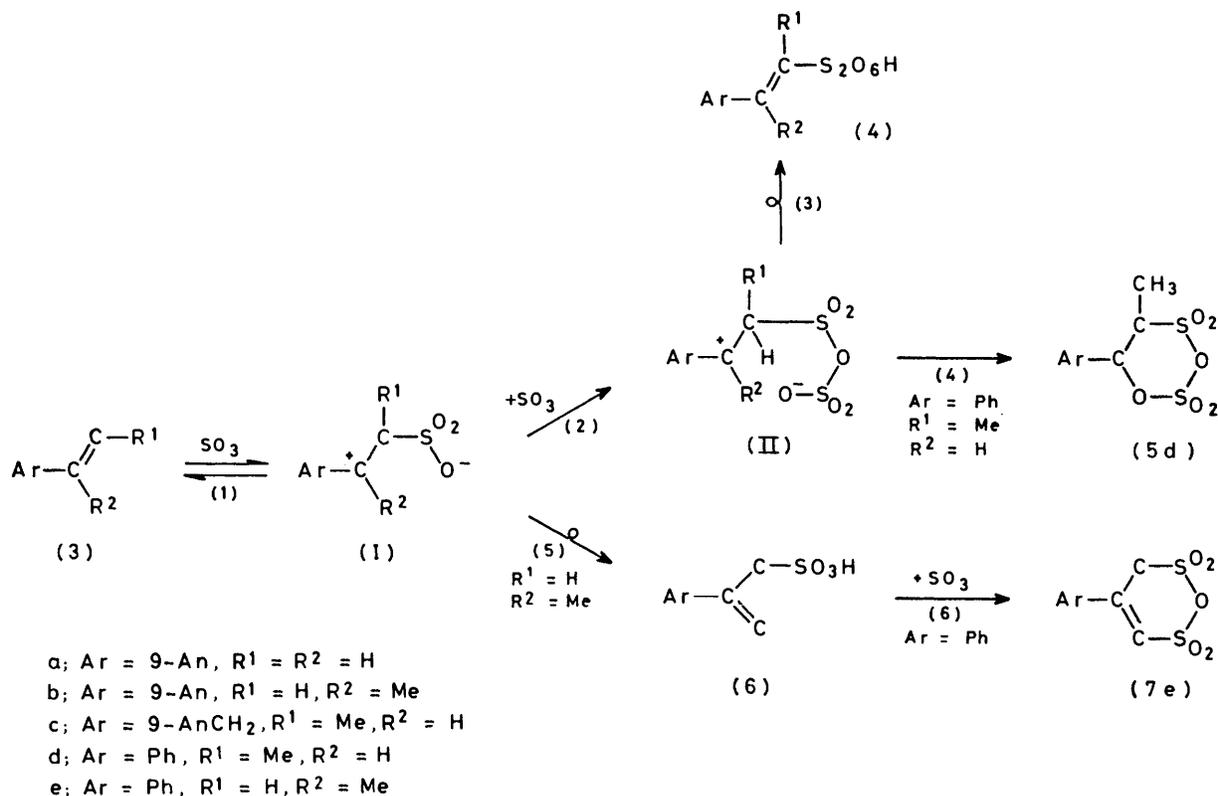
‡ The assignment of the three Fischer projections (2) was further proven by double-resonance experiment on the side-chain carbon-bonded hydrogens.

viously it was only reported that the sulphonation of prop-1-enylbenzene with dioxan-SO<sub>3</sub> in ethylene chloride yields 1-phenylprop-1-ene-2-sulphonate.<sup>9</sup>

**Prop-2-enylbenzene.**—The sulphonation of prop-2-enylbenzene leads to the formation of two products, viz. 92 ± 3% 2-phenylprop-1-ene-3-sulphonic acid (6e) \* and 8 ± 3% 2-phenylprop-1-ene-1-pyrosulphonic acid (4e) (see Scheme 1).† On using an excess of dioxan-SO<sub>3</sub> the disulphonic anhydride (7e) is obtained, which is thought to be formed by dehydration of 2-phenylprop-1-ene-1,3-disulphonic acid; this disulphonic acid would result from the sulphonation of the initially formed 2-phenylprop-1-ene-3-sulphonic acid. The presence of the compounds (6e) and (7e) was established

## DISCUSSION

**Mechanism of Product Formation.**—The formation of the products obtained in the reactions of 9-vinyl- (3a), 9-(prop-2-enyl)- (3b), and 9-[(*E*)-but-2-enyl]-anthracene (3c) and (*E*)-prop-1- and prop-2-enylbenzene (3d and e) with dioxan-SO<sub>3</sub> in dioxan may be explained in terms of the mechanism depicted in Scheme 1. The initial step is the transfer of SO<sub>3</sub> from the dioxan-SO<sub>3</sub> complex to the double bond with formation of (I). This dipolar intermediate cannot undergo an intramolecular proton shift of the hydrogen attached to the carbon carrying the pyrosulphonate to the sulphonate oxygen.‡ By analogy with



SCHEME 1

by field-ionization and field-desorption mass spectrometry. With these techniques signals were found at *m/e* 198 and 260 which agree with the molecular weights of compound (6e) and (7e), respectively. Moreover, the high-resolution mass measurement of (7e) (*Found*: *m/e*, 259.980. *Calc.* for C<sub>9</sub>H<sub>8</sub>S<sub>2</sub>O<sub>5</sub>: *M*, 259.9813). The products obtained on reaction of prop-2-enylbenzene with dioxan-SO<sub>3</sub> are similar to those reported by Suter.<sup>9</sup> The only difference is that Suter after working up, obtained 2-phenylprop-1-ene-1,3-disulphonate as principal product, which apparently results from hydrolysis of (7e).

\* The assignment of (6e) as a sulphonic acid is based on the use of 1 equiv. SO<sub>3</sub>.

† The configuration at the double bond could not be established in the absence of vinylic coupling but is thought to be *E* in view of the similarity in the chemical shifts of the β-hydrogens in (4a and e) (see Table 1).

aprotic aromatic sulphonation,‡ it is proposed that (I) reacts with SO<sub>3</sub> to give (II) [step (2)]. This intermediate can either undergo an intramolecular proton shift of the hydrogen attached to the carbon carrying the pyrosulphonate group with formation of the unsaturated pyrosulphonic acid (4) [step (3)], as observed with the substrates (3a—e), or give ring-closure [step (4)] with formation of cyclic sulphonate anhydrides, as observed on starting with (3e). In the case of substrates with the prop-2-enyl side-chain (3b and e), (I) may also undergo

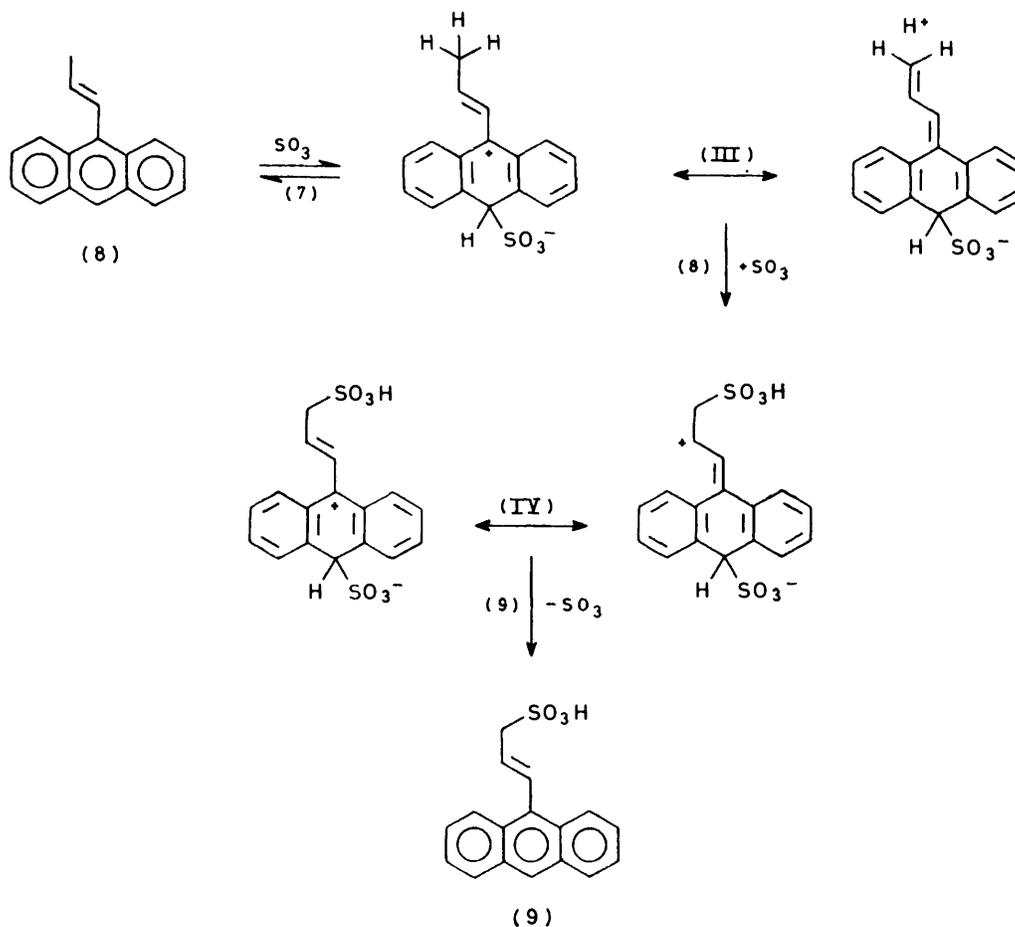
‡ A comparable geometric orientation exists in the 1-arenium-1-sulphonate σ-complex which results on reaction of *e.g.* *p*-dichlorobenzene with SO<sub>3</sub> in aprotic solvents.<sup>10</sup> This σ-complex does not allow an intramolecular proton shift. Instead it reacts with an additional molecule of SO<sub>3</sub> with formation of the 1-arenium-2-pyrosulphonate σ-complex which now undergoes an intramolecular proton shift with formation of the arenepyrosulphonic acid.

an intramolecular proton shift from the methyl group to the sulphonate oxygen *via* a six-membered transition state to yield (6) [step (5)]. An excess of dioxan-SO<sub>3</sub> leads to the formation of the anhydride (7) in the case of prop-2-enylbenzene, but not with 9-(prop-2-enyl)anthracene, possibly for steric reasons.

Substrate (3c) yields (*E*)- and (*Z*)-1-(9-anthryl)but-2-ene-3-pyrosulphonic acid [(*E*)- and (*Z*)-(4c), respectively] in a ratio of 0.28 : 1. The high yield of the *Z*-isomer is unexpected in view of the steric interaction between the sulpho and the anthryl group. It should be stressed that (*E*)-1-(9-anthryl)but-2-ene-1-sulphonic acid

The formation of sodium (*E*)-1-(9-anthryl)prop-1-ene-3-sulphonate (9) from 9-[(*E*)-prop-1-enyl]anthracene (8) may be explained as depicted in Scheme 2.\* In the first step SO<sub>3</sub> is transferred to the 10-position of anthracene [step (7)]. The resulting  $\sigma$ -complex (III) is stabilized by hyperconjugation, and has weakly acidic  $\gamma$ -hydrogens. Electrophilic sulphonation of one of these hydrogens yields the  $\sigma$ -complex (IV) [step (8)] which loses SO<sub>3</sub> with formation of the sulphonic acid [step (9)].

*Comparison with Related Substrates.*—The reaction of 9-ethylanthracene yields 1-(9-anthryl)ethane-1-sulphonic



SCHEME 2

is not formed in the reaction. This product would result from initial addition of SO<sub>3</sub> to the 10-position of anthracene followed by subsequent steps, as proposed for the formation of 1-(9-anthryl)propane-1-sulphonic acid from 9-propylanthracene [see steps (1), (3), and (6) in Scheme 2 of ref. 2]. The formation of (*E*)- and (*Z*)-(4c) together with the absence of (*E*)-1-(9-anthryl)but-2-ene-1-sulphonic acid suggests for substrate (3c) a higher reactivity at C- $\gamma$  of the isolated double bond compared with the 10-position of the anthryl group.

\* For a more complete discussion of the reactions depicted in Scheme 2, see ref. 2.

acid and (*E*)-(9-anthryl)ethylenepyrosulphonic acid.<sup>2</sup> The latter was also obtained as the sole product on reaction of 9-vinylanthracene with dioxan-SO<sub>3</sub>. The same product(s) is also formed in the reactions of 9-[(*E*)-prop-1-enyl]- and 9-propyl-anthracene, *viz.* (*E*)-1-(9-anthryl)prop-1-ene-3-sulphonic acid, and of 9-(prop-2-enyl)- and 9-isopropyl-anthracene, *viz.* both 2-(9-anthryl)prop-1-ene-3-sulphonic acid and 2-(9-anthryl)prop-1-ene-1-pyrosulphonic acid. The observation of these products supports the proposition that the three presently investigated substrates, *i.e.* 9-vinyl-, 9-[(*E*)-prop-1-enyl]-, and 9-prop-2-enyl-anthracene, are inter-

mediates in the dioxan-SO<sub>3</sub> reactions of 9-ethyl-, 9-propyl-, and 9-isopropyl-anthracene, respectively.

The sulphonation of both 9-vinylanthracene and vinylbenzene yielded, as for 9-(prop-2-enyl)anthracene and prop-2-enylbenzene, products with structurally identical side-chains, *viz.* 1-arylethylene-2-sulphonic acids\* for the vinyl derivatives, and 2-arylprop-1-ene-1-pyrosulphonic acids (5b and e) and 2-arylprop-1-ene-3-sulphonic acids (6b and e) for the prop-2-enyl derivatives. The formation of these products with the same side-chain structure illustrates that only the addition of SO<sub>3</sub> to the β-carbon of the side-chain [step (I), Scheme 1] leads to the formation of products.

The products formed in the sulphonation of 9-[(*E*)-prop-1-enyl]anthracene and (*E*)-prop-1-enylbenzene are completely different, *viz.* (*E*)-1-(9-anthryl)prop-1-ene-3-sulphonate and the cyclic sulphonate sulphate anhydride (5d), respectively. This difference may be explained in terms of the higher rate of SO<sub>3</sub> addition to the 10-position of the anthryl group (the subsequent reaction sequence, see Scheme 2, being fast) than to the β-carbon of the side-chain of 9-[(*E*)-prop-1-enyl]anthracene which itself is apparently higher than to the *p*-position of (*E*)-prop-1-enylbenzene.

#### EXPERIMENTAL

**Materials.**—9-Vinylanthracene and (*E*)-prop-1- and -2-enylbenzene were obtained from Aldrich. The reactions to obtain 9-[(*E*)-prop-1-enyl]-, 9-(prop-2-enyl)-, and 9-[(*E*)-but-2-enyl]-anthracene were carried out as described before;<sup>1,2</sup> the Grignard reactions yielded 9-alkenyl-9-hydroxy-9,10-dihydroanthracenes. 9-[(*E*)-Prop-1-enyl] and 9-(prop-2-enyl)-9-hydroxy-9,10-dihydroanthracene were found to dehydrate during their purification on a neutral alumina column; 9-[(*E*)-but-2-enyl]-9-hydroxy-9,10-dihydroanthracene was dehydrated as described before.<sup>1</sup> The

\* The reaction of vinylbenzene with dioxan-SO<sub>3</sub> complex in ethylene dichloride yielded, after basic hydrolysis, sodium 2-phenylethylene-1-sulphonate and sodium 2-hydroxy-2-phenylethanesulphonate.<sup>11</sup>

alkenylanthracenes were further purified by recrystallization from ethanol.

**Reaction Procedures.**—The reactions with dioxan-SO<sub>3</sub> complex have been carried out as described before.<sup>1</sup>

**<sup>1</sup>H N.M.R. Analysis.**—The spectra were recorded with a Varian HA-100 or XL-100 spectrometer; the chemical shifts (δ) of [<sup>2</sup>H<sub>8</sub>]dioxan solutions are relative to external, neat tetramethylsilane (capillary), and those of [<sup>2</sup>H<sub>8</sub>]dimethyl sulphoxide solutions relative to internal tetramethylsilane.

**Mass Spectroscopy.**—The field-ionization and field-desorption mass spectra were recorded on a Varian MAT 711 double-focusing mass spectrometer equipped with a combined e.i.-f.i.-f.d. source. For the f.d. experiments emission controlled f.d. was used at a threshold of 10 nA. The samples of the [<sup>2</sup>H<sub>8</sub>]dioxan solutions were loaded with the dipping technique. The f.i. measurements were obtained with a direct-insertion probe at 50 °C. Exact mass measurements were performed with a resolution of 10.000 (10% valley definition).

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