

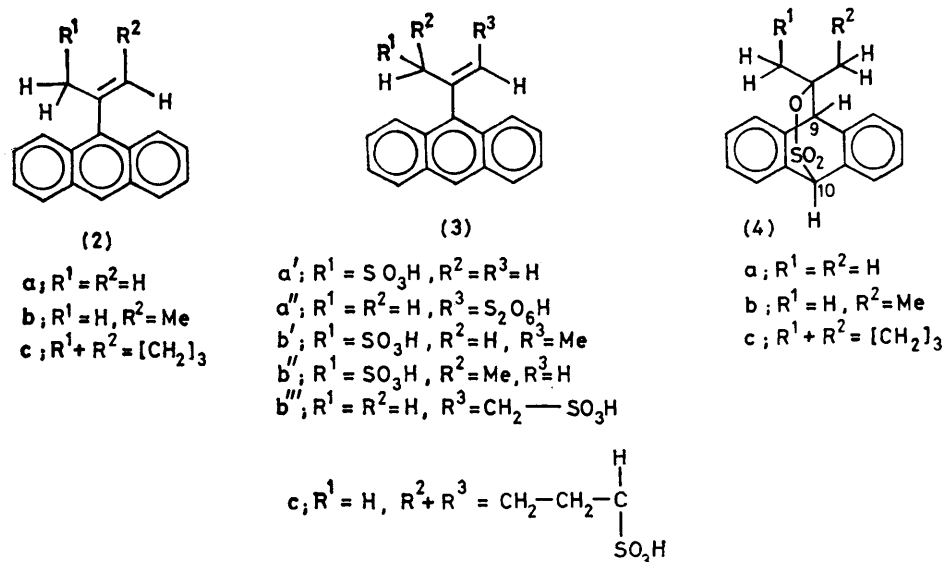
## Aromatic Sulphonation. Part 73.<sup>1</sup> Behaviour of Three 9-Alkylanthracenes containing One Side-chain $\alpha$ -Hydrogen in Dioxan-SO<sub>3</sub> Complex in Dioxan as Sulphonating Medium

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The reactions of 9-isopropyl-, 9-s-butyl-, and 9-cyclohexyl-anthracene with dioxan-SO<sub>3</sub> in dioxan at 17 °C lead to three types of products, viz. 9-alkenylanthracenes (2), unsaturated sulphonic acids (3), and seven-membered ring sultones (4). The 9-alkenylanthracenes (2) result from a redox reaction between the 9-alkylanthracenes and SO<sub>3</sub> and the unsaturated sulphonic acids (3) from the subsequent sulphonation of (2). The seven-membered ring sultones are formed from the  $\sigma$ -complex (resulting from addition of SO<sub>3</sub> to the 10-position of the original substrate) by a 1,2-hydride shift from the side-chain C- $\alpha$  to C-9.

THE reaction of 9-alkylanthracenes containing two side-chain  $\alpha$ -hydrogens with dioxan-SO<sub>3</sub> leads, depending on the structure of the alkyl group, to  $\alpha$ -alkylsulphonic acids and/or  $\alpha$ -alkene- $\gamma$ -sulphonic acids.<sup>1</sup> It was thought of

meric) products.† The reaction mixture of 9-isopropyl-anthracene (1a) with 1 equiv. dioxan-SO<sub>3</sub> after 20 min contained 45 ± 3% (1a), 17 ± 3% (2a), 29 ± 3% (3a'),‡ ca. 2% (3a''), and 7 ± 2% (4a); this composition remained



SCHEME 1 Products obtained in the reactions of 9-isopropyl-, 9-s-butyl-, and 9-cyclohexyl-anthracene with dioxan-SO<sub>3</sub>

interest to study some 9-alkylanthracenes with a secondary side-chain  $\alpha$ -carbon in order to determine the influence of the alkyl substituent at the side-chain  $\alpha$ -carbon.

### RESULTS

**Reactions with Dioxan-SO<sub>3</sub>.**—9-Isopropyl- (1a), 9-s-butyl- (1b), and 9-cyclohexyl-anthracene (1c) were treated with [<sup>2</sup>H<sub>8</sub>]dioxan-SO<sub>3</sub> complex in [<sup>2</sup>H<sub>8</sub>]dioxan at 17 °C. The mixtures obtained with these substrates contained three types of reaction products (see Scheme 1), viz. 9-alkenylanthracenes (2), unsaturated sulphonic acids (3), and seven-membered ring sultones (4), besides unchanged substrate and small amounts of unknown (probably poly-

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

‡ Product (3a') was proved<sup>1</sup> to be a sulphonic acid by the i.r. absorptions of the corresponding sulfonate (in KBr) which are at 1 200 (s), 1 040 (m), and 730 (m) cm<sup>-1</sup>.

§ The data in parentheses give the relative product yields.

constant for a reaction time of at least 90 min. The reaction mixture of 9-s-butylanthracene (1b) with 1.5 equiv. dioxan-SO<sub>3</sub> after 20 min contained 45 ± 3% (1b), 18 ± 2(32)% § (2b), 8 ± 2(15)% (3b'), 8 ± 2(15)% (3b''), 12 ± 2(23)% (3b'''), and 8 ± 2(15)% (4b). After 45 min the composition of the mixture was found to be 22 ± 2% (1b), 25 ± 2(32)% (2b), || 16 ± 2(20)% (3b'), § 12 ± 2(16)% (3b''), 17 ± 2(22)% (3b'''), || and 8 ± 2(10)% (4b).

The compositions of the reaction mixtures were determined by <sup>1</sup>H n.m.r. multicomponent analysis.<sup>3</sup> The structural assignment of the compounds obtained from

|| The configuration at the double bond could not be established in the absence of vinylic coupling. By analogy with the  $\alpha$ -ethylene- $\beta$ -sulphonic acid and the  $\alpha$ -alkene- $\gamma$ -sulphonic acids containing two vinylic hydrogens<sup>1</sup> it is thought that (3b') and (3b''') have the *E*-configuration. Evidence in favour of this reasoning is the similarity in the chemical shift of the vinylic hydrogens of (3b''') and (3c) the latter of which has, in view of the cyclohexenyl structure, the *E*-configuration (see Table). On the basis of a similar comparison between the chemical shift of the vinylic hydrogens of (2b and c), it seems very likely that (2b) has the *E*-configuration.

(1a and b) was based on their  $^1\text{H}$  n.m.r. signals (see Table). The structure of (2a) was further proven by comparison of its spectrum with that of an independently synthesized sample.<sup>4</sup> The structure of (4a) was assigned on the basis of its  $^1\text{H}$  n.m.r. chemical shifts in comparison with those of the sultones formed in the reaction of 1-chloro- and 1,5-dichloro-9-isopropylantracene with dioxan- $\text{SO}_3$ .<sup>5</sup> Further, the position of 10-H in (4a and b) ( $\delta$  5.74 and 5.75 respectively) is in agreement with that expected on the basis of the position of 9-H in 10-t-butyl-9,10-dihydroanthracene-9,10-sultone ( $\delta$  5.99).<sup>6</sup> The structures of (2b), (3b'), (3b''), and (3b''') have further been proven by double resonance experiments.

The mixture of 9-cyclohexylantracene (1c) with 1.5 equiv. dioxan- $\text{SO}_3$  after 20 min contained  $50 \pm 5\%$  (1c),  $15 \pm 3(30)\%$  (2c),  $30 \pm 4(60)\%$  (3c), and  $5 \pm 2(10)\%$  (4c). After 90 min the composition was:  $41 \pm 5\%$  (1c),  $13 \pm 3(21)\%$  (2c),  $42 \pm 4(71)\%$  (3c), and  $4 \pm 2(7)\%$  (4c). The structures of (2c) and (3c) are based only on the absorptions of  $\beta$ -H at  $\delta$  5.91 and 6.12 respectively which values are in good agreement with those obtained for the corresponding proton of (2a) ( $\delta$  5.89; the other vinylic hydrogen absorbs at  $\delta$  5.27) and (2b) ( $\delta$  6.28) for (2c), and of (3a) ( $\delta$  5.78 and 6.50) and (3b) ( $\delta$  5.92) for (3c). The assignment of the structure of (4c) is based on the positions of 9- and 10-H which are in good agreement with those of (4a and b).

The positively assigned  $^1\text{H}$  n.m.r. data of all the reported compounds are listed in the Table.

$^1\text{H}$  N.m.r. data of the substrates and products in [ $^2\text{H}_6$ ]dioxan

Compound	$\delta$					
	$\alpha$ -H <sup>a</sup>	$\beta$ -H <sup>a</sup>	$\gamma$ -H <sup>a</sup>	$\alpha'$ -H <sup>a</sup>	9-H <sup>b</sup>	10-H <sup>b</sup>
(1a)	4.77 (1 H, m)	1.87 (3 H, d)		1.87 (3 H, d)		8.50 (s)
(1b)	4.49 (1 H, m)	2.37 (2 H, m)	0.99 (3 H, t)	1.85 (3 H, d)		8.52 (s)
(1c)	4.29 (1 H, t)					8.43 (s)
(2a)		5.27 (1 H, s) 5.89 (1 H, s)		2.37 (3 H, s)		8.50 (s)
(2b)		6.28 (1 H, q)	1.41 (3 H, d)	2.33 (3 H, s)		ca. 8.6 (s)
(2c)		5.91 (s)				
(3a')		5.78 (1 H, s) 6.50 (1 H, s)		4.59 (2 H, s)		8.60 (s)
(3a'')		6.86 (1 H, s)		2.81 (3 H, s)		
(3b')		6.86 (1 H, q)	1.55 (3 H, d)	5.22 (2 H, s)		8.61 (s)
(3b'')		ca. 4.5	1.94 (3 H, d)	5.85 (1 H, s)		8.61 (s)
(3b''')		5.92 (1 H, t)	ca. 4.5	2.45 (3 H, s)		8.61 (s)
(3c)		6.12 (d)				8.55 (s)
(4a)		1.53 (3 H, s)		1.53 (3 H, s)	4.10 (1 H, s) <sup>c</sup>	5.74 (1 H, s) <sup>c</sup>
(4b)		ca. 2.2	ca. 1.1	1.48 (3 H, s)	4.15 (1 H, s) <sup>c</sup>	5.75 (1 H, s) <sup>c</sup>
(4c)					3.99 (1 H, s) <sup>c</sup>	5.68 (1 H, s) <sup>c</sup>

<sup>a</sup>  $\alpha$ ,  $\beta$ , etc. refers to the side-chain carbon. These carbons are numbered according to:  $\alpha'$ C-(C $\alpha$ -Ar)-C $\beta$ -C $\gamma$ . Further with (2a), (3a'), and (3a'')  $\beta$ -C represents the double bonded carbon. The side-chain hydrogens other than those specifically listed yield for (1c) a multiplet at  $\delta$  1.9–2.7, and for (2c) and (3c) a multiplet at  $\delta$  1.5–2.6. <sup>b</sup> 2-, 3-, 6-, 7-H of all the anthracene derivatives give a multiplet of total width of ca. 15 Hz, centred at  $\delta$  7.60  $\pm$  0.05, and 4- and 5-H a ca. 15 Hz multiplet centred at  $\delta$  8.14  $\pm$  0.05. 1- and 8-H exhibit a ca. 15 Hz multiplet centred for the substrates at  $\delta$  8.65  $\pm$  0.05, for (2a) at  $\delta$  8.27, for (3a') at  $\delta$  8.39, for (2b) and (3b', b'', and b''') at  $\delta$  8.19, and for (3c) at  $\delta$  8.13 and 8.31. <sup>c</sup> 9- and 10-H of the sultones represent the hydrogens attached to the central ring, at the side of the alkyl group and the  $\text{SO}_2$  group, respectively.

## DISCUSSION

The reaction of the three investigated substrates with dioxan- $\text{SO}_3$  yields 9-alkenylantracenes (2), unsaturated sulphonic acids (3), and seven-membered ring sultones (4). The formation of (2) and (4) may be explained as depicted in Scheme 2 for 9-isopropylantracene. The unsaturated sulphonic acids are thought to result from the sulphonation of the unsaturated hydrocarbons (2).

The formation of (2) may be explained in terms of steps (1)–(3) which are identical to those suggested in

the preceding paper for the formation of the 9-alkenylantracene, proposed as an intermediate in the reaction of the 9-alkylantracenes, containing two side-chain  $\alpha$ -hydrogens, with dioxan- $\text{SO}_3$ .<sup>1</sup>

Product (4) is formed by the steps (1), (4), and (5). Step (4) represents a 1,2-hydride shift from the side-chain  $\alpha$ -carbon to C-9. A related 1,2-methyl shift, but with [ $^2\text{H}_6$ ]dimethyl sulphoxide as solvent, was reported for the rearrangement of 10-t-butyl-9,10-dihydroanthracene-9,10-sultone into 9-methyl-9-(prop-2-enyl)-9,10-dihydroanthracene-10-sulphonic acid.<sup>8</sup> Ring closure of the resulting dipolar structure then yields the sultone (4) [step (5)].

In the  $\sigma$ -complex (I) there exists, in view of the planarity at the  $sp^2$  C-9 atom, steric repulsion between the alkyl side-chain and 1- and 8-H on the one hand, and of the sulphonate group and 4- and 5-H on the other. Both steps (2) and (4) are accompanied by relief of the steric strain, as the central ring of (II) will have a *cis* 'boat' or 'butterfly' structure as in 9-isopropylidene-10-isopropyl-9,10-dihydroanthracene,<sup>7</sup> and that of (III) a non-planar boat structure similar to that of 9,10-dialkyl-9,10-dihydroanthracene.<sup>8</sup>

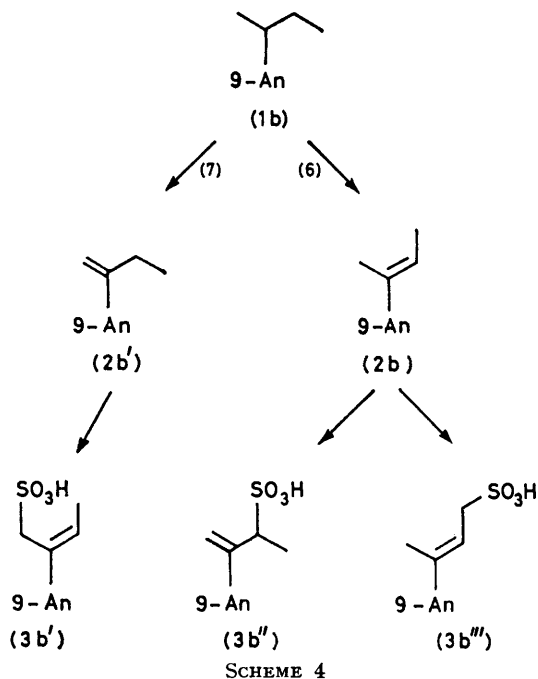
The only difference between the reactions of 9-alkylantracenes containing two side-chain  $\alpha$ -hydrogens<sup>1</sup> and

9-isopropyl-, 9-s-butyl-, and 9-cyclohexyl-anthracene with dioxan- $\text{SO}_3$  complex is the formation of the sultones (4) with the latter series of substrates. The absence of sultone formation with the former substrates may be due to the improbability of the hydride shift [step (4)] which would yield a secondary carbenium ion which is less stable than the preceding 'tertiary' one.

Evidence in favour of the presumed intermediacy of 9-alkenylantracenes (2) in the formation of the unsaturated sulphonic acids (3) is (i) the formation of



The low rate of sulphonation of (2b and c) is not only apparent from the detection of these intermediates in the reaction of (1b and c), respectively, but that of (2c) also from the change in composition of the reaction mixture of



9-cyclohexylanthracene with time [the ratio of (2c) to (3c) after 20 and 90 min being 0.50 and 0.30, respectively].

The reaction of 9-cyclohexylanthracene with dioxan-SO<sub>3</sub> yields only the  $\alpha$ -alkene- $\gamma$ -sulphonic acid (2b). The absence of products homologous with (3a', a'', b', and b'') is probably due to the steric interaction between the side-chain and 1- and 8-H.

#### EXPERIMENTAL

**Materials.**—The three 9-alkylanthracenes have been synthesized by reaction of anthrone with a three-fold excess

of the appropriate Grignard reagent.<sup>10</sup> 9-Hydroxy-9-isopropyl-9,10-dihydroanthracene was found to dehydrate under the reaction conditions with formation of the desired 9-isopropylanthracene, but in reactions leading to 9-s-butyl- and 9-cyclohexyl-anthracene the 9-alkyl-9-hydroxy-9,10-dihydroanthracenes were obtained as such (*cf.* ref. 11). The dihydroanthracenes were purified by chromatography on neutral alumina (eluant benzene), followed by recrystallization from light petroleum (b.p. 40–60°). They (0.04 mol) were dehydrated by heating them with phosphorus pentoxide (0.07 mol) in carbon tetrachloride (150 ml) at 70 °C for 2 h.<sup>11b</sup> The solution was decanted, washed with water, and dried (MgSO<sub>4</sub>). 9-Alkylanthracenes were purified as described before.<sup>1</sup>

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

**Spectral Analysis.**—<sup>1</sup>H N.m.r. spectra were recorded with a Varian HA-100 or XL-100 spectrometer; chemical shifts ( $\delta$ ) are relative to external tetramethylsilane (capillary). I.r. spectra (KBr) were recorded with a Perkin-Elmer 177 spectrometer.

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