Aromatic Sulphonation. Part 72.[1] Behaviour of Some 9-Alkylanthracenes containing 2 α-Hydrogens and 0—3 β-Hydrogens in the Side-chain with Dioxan–Sulphur Trioxide in Dioxan as Sulphonating Medium; Mechanism for Alkyl Side-chain Reduction and Subsequent Sulphonation

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The reactions at 17 °C of seven 9-alkylanthracenes, with two alkyl α-hydrogens, with dioxan–SO_3 in dioxan has been studied. With the exception of 9-ethyl- and 9-neopentyl-anthracene these substrates yield products having a side-chain structure with (i) the sulphonate group at C-α (α-sulphonic acids) and/or (ii) a double bond at C-α with the sulphonate group at C-γ (α-alkene-γ-sulphonic acids). 9-Ethylanthracene yields, besides the α-sulphonic acid, an α-alkene-β-sulphonic acid, whereas 9-neopentylanthracene leads to sulphonation of the anthryl group at the 10- and 4-positions. It is proposed that the α-sulphonic acids are formed as suggested for the formation of 9-anthrylmethanesulphonic acid from 9-methylanthracene, and that the α-alkene-γ-sulphonic acids are produced by sulphonation of 9-(alk-1-enyl)anthracenes, which intermediates result from a redox reaction between the 9-alkylanthracenes and SO_3.

THE sulphonation of 9-methylanthracene with dioxan–SO_3 unexpectedly yielded 9-anthrylmethanesulphonic acid as the only product.[2] Accordingly it was thought of interest to study a number of other 9-alkylanthracenes.

Two other examples of side-chain reactions of a 9-methylanthracene have been reported.[3] Nonhebel observed that 9-methylanthracene underwent bromination both under radical and ionic conditions to give only 9-bromo-10-methylanthracene, but that bromination of 2,9-dimethylanthracene with bromine in carbon tetrachloride (radical conditions) gave exclusively 9-bromomethyl-2-methylanthracene.[3a] Suzuki found a ready side-chain nitration of 9-methylanthracene to yield nearly quantitatively 9-nitromethylanthracene.[3b] The behaviour of 9-ethylanthracene was, however, strikingly different from that of the 9-methyl analogue, since it yielded 9-ethyl-10-nitroanthracene and 9-ethyl-9-hydroxy-10-nitro-9,10-dihydroanthracene, *i.e.* did not undergo side-chain substitution.

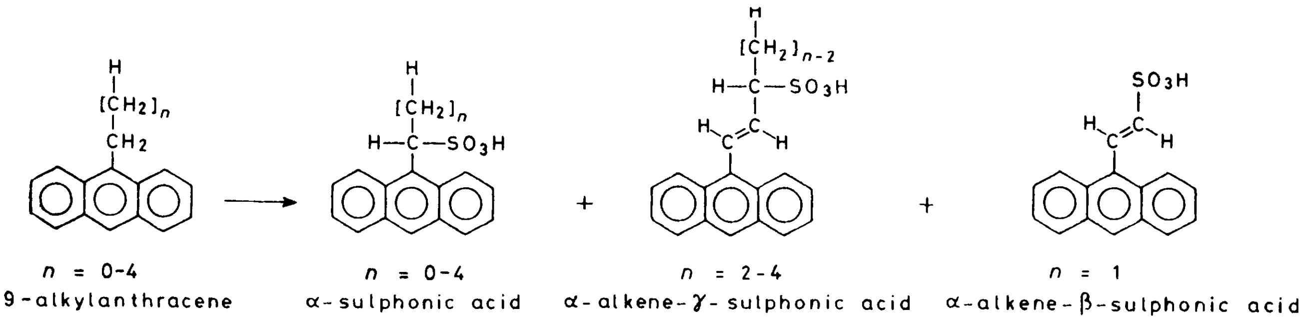
RESULTS

Reactions with Dioxan–SO_3.—The 9-alkylanthracenes were treated with $[^2H_8]$dioxan–SO_3 complex in $[^2H_8]$dioxan at 17 °C. The composition of the mixtures was determined both during the reaction and after the reaction was completed (*ca.* 45 min) by ^1H n.m.r. multicomponent analysis.[4,†] The final composition of these mixtures remained the same for at least one week. In all reactions small amounts of unknown (probably polymeric) products were formed, the amount of which increased with an increasing amount of dioxan–SO_3 complex.

TABLE 1

Side-chain sulphonation of 9-alkylanthracenes in $[^2H_8]$-dioxan at 17 °C

Alkyl group	Equiv. SO_3 (±10%)	Yield (%) α-Sulphonic acid	α-Alkene-β-sulphonic acid	α-Alkene-γ-sulphonic acid	Unconverted substrate
Ethyl	1	50	*ca.* 2		48
	2	77	23		
Propyl	1	18		19	63
	2	31		47	22
Butyl	1	20		18	62
Pentyl	1	4		36	60
Isobutyl	1			25	75
Isopentyl	1	*ca.* 2		40	58



SCHEME 1

9-(*n-Alkyl*)*anthracenes*. The reaction of 9-ethylanthracene with dioxan–SO_3 yielded 1-(9-anthryl)ethane-1-sulphonic acid and (*E*)-(9-anthryl)ethylenesulphonic acid (see Scheme 1 and Table 1). The formation of this unsaturated sulphonic acid was established on the basis of the close resemblance of its spectrum with that of the sulphonating mixture of 9-vinylanthracene.[5] The reactions of 9-propyl-, 9-butyl-, and 9-pentyl-anthracene with dioxan–SO_3 gave mixtures consisting of unconverted substrate and two different types of sulphonic acids, *viz.* α-sulphonic acids and

† In the reactions of these substrates with $[^1H_8]$dioxan–SO_3 complex in $[^1H_8]$dioxan no dioxan decomposition products [2] were found.

α-alkene-γ-sulphonic acids (see Scheme 1 and Table 1).

The structures of the α-sulphonic acids have been assigned on the basis of the ^1H n.m.r. spectra. Molecular models of 1-(9-anthryl)alkane-1-sulphonic acids revealed that there is strong steric repulsion between the α-alkyl hydrogen(s) and the hydrogens at C-1 (or C-8) on the one side, and between the β-alkyl hydrogens and the hydrogens at C-8 (or C-1) on the other. Both these steric repulsions were apparent from the nuclear Overhauser enhancements (NOE) which with *e.g.* sodium 1-(9-anthryl)ethane-1-sulphonate amounted to 22 and 10%, respectively. Due to these steric interactions the hydrogens at C-1 and -8 are not equivalent and are likely to have different chemical shifts, as observed for all the α-sulphonic acids obtained (Table 2). These results illustrate that C-9–C-α bond rotation is slow on the n.m.r. time scale at the probe temperature.

The structure of the α-alkene-γ-sulphonic acid portion of the various compounds has been assigned from the ^1H n.m.r. spectra (Table 3), and has been proven by double and triple resonance. All the α-alkene-γ-sulphonic acids have a vinyl coupling constant of 16 Hz and accordingly have the *E*-configuration.

Branched 9-alkylanthracenes. Three branched 9-alkylanthracenes have been investigated containing two side-chain α-hydrogens, *viz.* 9-isopentyl-, 9-isobutyl-, and 9-neopentyl-anthracene which contain two, one, and zero side-chain β-hydrogens, respectively. 9-Isopentylanthracene gave products corresponding to those of the n-alkylanthracenes (Table 1), but 9-isobutylanthracene yielded only the α-alkene-γ-sulphonic acid derivative. The configuration at the double bond of this product could not be established in the absence of an observable vinyl coupling.

The sulphonation of 9-neopentylanthracene with *ca.* 1.5 equivalents of dioxan–SO_3 leads only to anthryl sulphonation products, *viz.* 85% 9-neopentylanthracene-10-sulphonic acid, δ([$^2H_8$]dioxan), 9.54 (1 H, s) and 9.45 (1 H, s) (4- and 5-H), 8.68 (1 H, s) and 8.77 (1 H, s) (1- and 8-H), and 7.1—7.5 (4 H, m, 2-, 3-, 6-, and 7-H), and 15% 9-neopentylanthracene-4-sulphonic acid (based only on the singlet at δ 9.25 assigned to 10-H). The sulphonation of this substrate is slower than the others investigated: for completion of the reaction 90 min at 40 °C are required.

Spectral Properties.—^1H N.m.r. data of the α-sulphonic acid, the unsaturated sulphonic acids, and the substrates are given in Tables 2—4 respectively. In order to check whether the salts resulting from the reactions of 9-ethyl-

TABLE 2

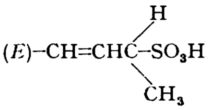
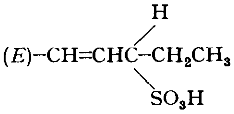
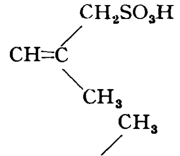
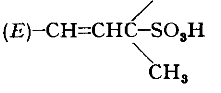
^1H N.m.r. data of the α-sulphonic acids of 9-alkylanthracenes in [$^2H_8$]dioxan

	δ						
Alkyl group	1-H [a]	8-H [a]	α-H [b]	β-H [b]	γ-H [b]	δ-H [b]	ε-H [b]
Ethyl	8.59 (m)	9.00 (m)	6.27 (1 H, q)	2.32 (3 H, d)			
Propyl	8.48 (m)	8.97 (m)	6.06 (1 H, m)	2.96 (2 H, m)	0.90 (3 H, t)		
Butyl	8.50 (m)	9.04 (m)	6.15 (1 H, m)	2.95 (2 H, m)	1.36 (2 H, m)	0.90 (3 H, t)	
Pentyl	8.45 (m)	9.03 (m)	6.14 (1 H, m)	2.95 (2 H, m)	2.00 (2 H, m)	1.45 (2 H, m)	0.86 (3 H, t)
Isopentyl [c]		8.93 (m)	*ca.* 6.1 (m)	*ca.* 2.8 (m)		0.8 (d)	

[a] 2-, 3-, 6-, and 7-H of all the anthracenes give a multiplet of a total width *ca.* 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, the α-sulphonic acids and the unsaturated sulphonic acids is at 8.48 ± 0.04, 8.68 ± 0.07, and 8.56 ± 0.05 respectively. [b] α, β, *etc.*, refer to side-chain carbons. [c] Present in trace amounts; only the positively assigned absorptions are listed.

TABLE 3

^1H N.m.r. data of the unsaturated sulphonic acids obtained from 9-alkylanthracenes in [$^2H_8$]dioxan

	δ					
Anthracene substituent at position 9	1- and 8-H [a]	α-H [b]	β-H [b]	γ-H [b]	δ-H [b]	ε-H [b]
(*E*)–$CH{=}CHSO_3H$	8.37 (m)	8.61 (1 H, d) [c]	7.26 (1 H, d) [c]			
(*E*)–$CH{=}CHCH_2SO_3H$	8.48 (m)	*ca.* 7.6 (1 H, d) [d]	6.26 (1 H, dt)	4.46 (2 H, d)		
 (*E*)–$CH{=}CHCH(CH_3)SO_3H$	8.50 (m)	*ca.* 7.6 (1 H, d) [d]	6.26 (1 H, dd)	4.48 (1 H, m)	1.93 (3 H, d)	
 (*E*)–$CH{=}CHCH(SO_3H)CH_2CH_3$	8.45 (m)	*ca.* 7.6 (1 H, d) [d]	6.13 (1 H, dd)	4.23 (1 H, dt)	2.50 (2 H, m)	1.39 (3 H, t)
 $CH{=}C(CH_2SO_3H)CH_3$	8.35 (m)	7.41 (1 H, s)		4.47 (2 H, s) [e]	1.76 (3 H, s)	
 (*E*)–$CH{=}CHC(CH_3)_2SO_3H$	8.38 (m)	*ca.* 7.6 (1 H, d) [d]	6.35 (1 H, d) [c]		1.91 (6 H, s)	

[a,b] As Table 2. [c] *J* 16 Hz. [d] This doublet (*J* 16 Hz) is not apparent from the ^1H n.m.r. spectrum of the [$^2H_8$]dioxan solution, but only in that of the solution of the isolated sodium sulphonate in [$^2H_6$]dimethyl sulphoxide (see Experimental section). [e] γ-C represents the carbon carrying the sulphonic acid group.

TABLE 4

^{1}H N.m.r. data of 9-alkylanthracenes in [^{2}H$_8$]dioxan

	δ					
Alkyl group	1- and 8-H [a]	α-H [b]	β-H [b]	γ-H [b]	δ-H [b]	ε-H [b]
Ethyl	8.42 (m)	3.75 (2 H, q)	1.49 (3 H, t)			
Propyl	8.40 (m)	3.70 (2 H, m)	1.92 (2 H, m)	1.19 (3 H, t)		
Butyl	8.45 (m)	3.73 (2 H, m)	1.94 (2 H, m)	1.63 (2 H, m)	1.07 (3 H, t)	
Pentyl	8.45 (m)	3.63 (2 H, m)	←	1.4—2.0 (6 H, m)	→	1.07 (3 H, t)
Isobutyl	8.45 (m)	3.61 (2 H, d)	1.83 (1 H, m)	1.14 (6 H, d)		
Isopentyl	8.38 (m)	3.68 (2 H, d)	1.77 (2 H, m)	1.96 (1 H, m)	1.16 (6 H, d)	
Neopentyl	8.55 (m)	3.85 (2 H, s)		1.14 (9 H, s)		

[a, b] See the corresponding subscripts of Table 2.

and 9-isobutyl-anthracene with dioxan–SO$_3$ are sulphonates (and *e.g.* not sulphates) the i.r. spectra of the isolated sodium salts (in KBr) have been recorded. They showed absorptions at 1 200s, 1 040m, and 730m cm^{-1}. These values correspond with the ranges suggested by Colthup[6] for sulphonic acids and sulphonate salts, *viz.* 1 260—1 150s, 1 080—1 010m, and 700—600m cm^{-1}. The sodium salts of the sulphonation products of 9-ethyl- and 9-isobutyl-anthracene have been isolated from the residues obtained by working up the reaction mixtures (see Experimental section) by extraction with hot ethanol.

DISCUSSION

The sulphonation of the presently studied 9-alkylanthracenes leads, depending on the structure of the alkyl group, in general to α-sulphonic acids and α-alkene-γ-sulphonic acids. Their formation may be explained in terms of the mechanism * depicted in Scheme 2.

The α-sulphonic acids are formed *via* steps (1), (3), and (6) which are similar to those suggested for the side-chain sulphonation of 9-methylanthracene.[2] The α-alkene-γ-sulphonic acids may be formed in two stages. The first one is the formation of a 9-(alk-1-enyl)-anthracene in a redox (type) reaction (4) in which hexavalent sulphur is reduced to tetravalent sulphur. The second one is sulphonation of the 9-(alk-1-enyl)-anthracenes by steps (8)—(10).

It is likely that the redox reaction (4) is preceded by the proton shift (2), as the required electron transfer is more difficult with (I) (where the electron is transferred towards the negative charge of the sulphonate group) than with (II). The proton shift (2) is probably intramolecular in view of the geometric orientation of the α-alkyl hydrogen and the sulphonate group, especially if the structure of the intermediate (I) tends to the *cis* ' boat ' or ' butterfly ' structure established for 9-isopropyl-10-isopropylidene-9,10-dihydroanthracene.[11] The alternative redox reaction (7) of (III) leading to the side-chain reduced structure (IV) cannot be ruled out, but is thought improbable in view of the stability of the 9-alkylanthracene-α-sulphonic acids formed under the sulphonation conditions.

As for steps (1) and (8) the dioxan–SO$_3$ complex transfers sulphur trioxide predominantly to the 10-position of 9-alkyl- and 9-(alk-1-enyl)-anthracene, because of the high reactivity of the 9- and 10-positions (*cf.* ref. 12) as a result of the hyperconjugative stabilization of the resulting σ-complexes (I) and (IV) by the alkyl and the alkenyl group, respectively. This hyperconjugation enhances the acidity of the α-hydrogens of the alkyl group of (I) and of the γ-hydrogens of the alk-1-enyl group of (IV) and renders both more susceptible towards sulphonation [steps (3) and (9) respectively].†

Treatment of 9-methyl-, 9-ethyl-, and 9-propyl-anthracene with FSO$_3{}^2$H [9] leads to stable [10-^{2}H]-9-alkyl-10-anthracenium ions which did not undergo D–H exchange of the α-alkyl hydrogens. This result would imply that the sulphonation step (3), and probably also step (9), proceeds by electrophilic substitution (S_E2) and not by initial proton loss and subsequent sulphur trioxide addition, *e.g.* steps (2) and (5). Accordingly steps (2) and (3) are competitive and determine the ratio of the α-sulphonic and α-alkene-γ-sulphonic acids.

Because of the electron-withdrawing effect of the sulphoalkyl substituent the σ-complexes (III) and (V) lose sulphur trioxide with formation of sulphonic acids [steps (6) and (10), respectively]. No products resulting from the alternative, *i.e.* loss of 10-H, have been observed. In fact, this proton-removing step will be relatively slow in view of the strong steric repulsion between the sulphonate group and the *peri*-hydrogens in anthracene-9-sulphonic acid. This is apparent (i) from the maximal kinetic isotope effect of hydrogen for the formation of *meso*-sulphonic acid from [9-^{2}H]anthracene,[14]

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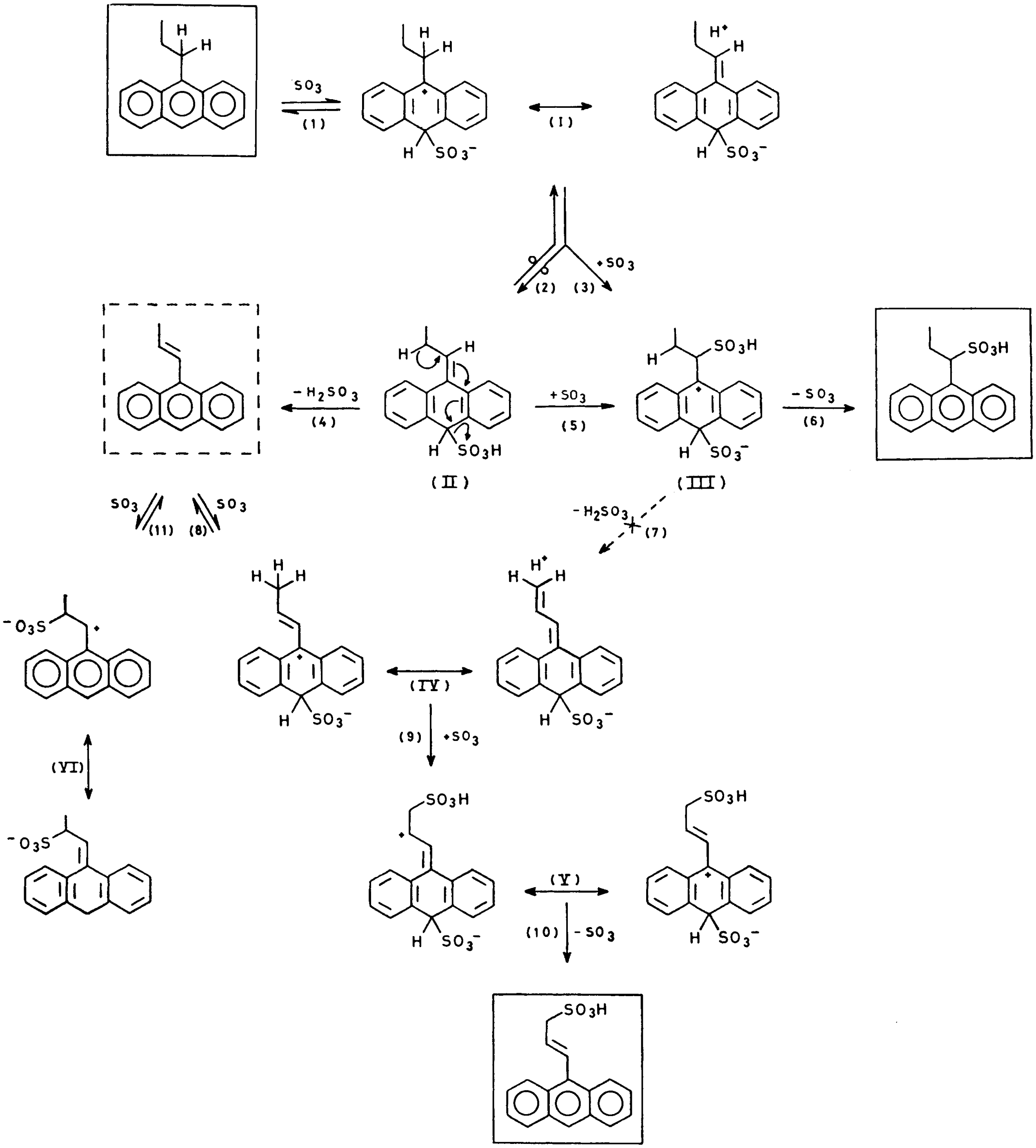
* The possibility of initial electron-transfer from the substrate to SO$_3$ with formation of a radical cation of the substrate was considered to be highly unlikely in view of the following evidence. First, in the reaction of 9-methylanthracene with dioxan–SO$_3$ (*cf.* ref. 2) no dimeric products such as 1,2-di-(9-anthryl)ethane were formed. This indicates the absence of 9-anthrylmethyl radical which should have been formed from the radical cation obtained in an initial electron-transfer oxidation by proton loss (*cf.* ref. 7). Secondly, in the sulphonation of 9-alkylanthracenes with side-chains other than methyl no secondary α-(9-anthryl)alkyl radical, which should be an intermediate leading to a side-chain substituted product, is obtained from the radical cations by proton loss. This can be concluded from the absence of side-chain substituted products in the reaction of 9-ethyl- and 9-isopropyl-anthracene with copper(II) bromide in methanol.[7] The absence of proton loss was ascribed [7] to the steric interaction in the resulting α-(9-anthryl)alkyl radical between the substituents at the α-carbon and the hydrogens at C-1 and -8, as the *p*-orbital containing the unpaired electron prefers to be perpendicular to the plane of the anthracene rings. Thirdly, anthracene [8] and 9-methyl-, 9-ethyl-, and 9-propyl-anthracene are protonated prior to their oxidation by fluorosulphuric acid.[9] Fluorosulphuric acid is as strong an oxidizing agent as SO$_3$.[10]

† The far less acidic hydrogens of aliphatic hydrocarbons are for example, very difficult to sulphonate.[13]

and (ii) from the relatively very high rate of desulphonation of anthracene-9-sulphonic acid.[15]

Step (11) represents the transfer of SO_3 from the dioxan–SO_3 complex to the double bond of the 9-(alk-1-enyl)anthracene. This route does not lead to the formation of products as can be seen from the absence of ' direct ' double-bond sulphonation products in the reaction of 9-(prop-1-enyl)anthracene with dioxan–SO_3. Step (11) does, however, represent the first step in the formation of (*E*)-(9-anthryl)ethylenesulphonic acid from 9-vinylanthracene (for a discussion on this subject see ref. 5).

Unfortunately the concentrations of the σ-complexes and the 9-(alk-1-enyl)anthracene intermediates were found to be below the limits of ^1H n.m.r. detection for all substrates in the present study, rendering the direct



Scheme 2

proof of the proposed mechanism (Scheme 2) impossible. However there is indirect evidence in favour of the proposed mechanism. First, in the reaction of 9-isopropylanthracene with dioxan–SO_3 complex 9-(prop-2-enyl)anthracene was detected as an intermediate,[16] and further sulphonation of this hydrocarbon proper does lead to the same products, *viz.* 2-(9-anthryl)prop-1-ene-3-sulphonic acid and 2-(9-anthryl)prop-1-ene-1-pyrosulphonic acid.[5] The latter substrate only requires a smaller amount of SO_3 than 9-isopropylanthracene. Also in the reactions of 9-propyl- and 9-(prop-1-enyl)-anthracene[5] with dioxan–SO_3 a mutual product is obtained, *viz.* 1-(9-anthryl)prop-1-ene-3-sulphonic acid.* The last compound is the proposed intermediate in the formation of the α-alkene-γ-sulphonic acid from 9-propylanthracene (steps 1, 2, and 4 of Scheme 2). The observation of the formation of the mutual sulphonic acids in the reactions of 9-isopropyl- and 9-(prop-2-enyl)-anthracene, as well as in 9-propyl- and 9-(prop-1-enyl)-anthracene, seems to prove the two-stage character of the formation of the unsaturated sulphonic acids from the 9-alkylanthracenes. Secondly 9-neopentylanthracene (with no γ-hydrogen, see also below) and 9-t-butylanthracene (with no α-hydrogen) should, in view of their alkyl structure, lead to products different from those predicted by Scheme 2. This is in fact observed, as 9-neopentylanthracene yields a mixture of 9-neopentylanthracene-10- and -4-sulphonic acids, and 9-t-butylanthracene yields 10-t-butyl-9,10-dihydroanthracene-9,10-sultone.[17]

The investigated substrates containing an alkyl side-chain with two α- and β-hydrogens and at least one γ-hydrogen, *viz.* 9-propyl-, 9-butyl-, 9-pentyl-, and 9-isopentyl-anthracene on reaction with dioxan–SO_3 yield both an α-sulphonic acid and an α-alkene-γ-sulphonic acid. 9-Ethylanthracene also yields an α-sulphonic acid, but further (*E*)-(9-anthryl)ethylenesulphonic acid which results from sulpho-deprotonation of 9-vinylanthracene produced by a redox reaction.[5]

The very low yield of α-sulphonic acid formed in the reaction of 9-isopentylanthracene with dioxan–SO_3 may be explained in terms of the large steric hindrance for step (3) and/or (5), mainly due to the interaction of the incoming sulphur trioxide with the *peri*-hydrogens 1- and 8-H [which prevents the formation of the homologue of (III)]. This steric hindrance is even larger for 9-isobutylanthracene (with two α- and one β-hydrogen) which in fact yields no α-sulphonic acid but only 1-(9-anthryl)-2-methylprop-1-ene-3-sulphonic acid, *i.e.* an α-alkene-γ-sulphonic acid. For the same reason no α-sulphonic acid is formed in the reaction of 9-isopropyl-, 9-s-butyl-, and 9-cyclohexyl-anthracene with dioxan–SO_3.[16] Replacement of the β-hydrogen of the side-chain of 9-isobutylanthracene by methyl [leading to 9-neopentylanthracene (with two α- and no β-hydrogen)] will greatly reduce the rate of step (4), since the rate is very much lower for a Me^+ than a proton transfer. In fact, with 9-neopentylanthracene only sulphonation at the 10- and 4-positions of the anthryl group is observed, *viz.* in a ratio of 85 : 15. It should be stressed that with none of the other substrates reported in this and the following papers[5,16] have any anthryl-substituted sulphonic acids been observed.

Further oxidation by a second redox reaction of the 9-(alk-1-enyl)anthracenes formed from 9-pentyl- and 9-cyclohexyl-anthracene by step (4) would yield a 9-(alka-1,3-dienyl)anthracene which upon reaction with dioxan–SO_3 would form an α,γ-alkadiene-ε-sulphonic acid side-chain derivative. On the basis of the absence of 1-(9-anthryl)penta-1,3-diene-5-sulphonic acid and 1-(9-anthryl)cyclohexa-1,3-diene-5-sulphonic acid in the reaction mixtures of 9-pentyl- and 9-cyclohexyl-anthracene, respectively,[16] it is concluded that this further oxidation does not occur.

EXPERIMENTAL

Materials.—The 9-alkylanthracenes have been synthesized as follows.[18,†] Anthrone in warm benzene was added dropwise to a stirred solution of the appropriate Grignard reagent (3 equiv.) in dry ether. After the addition was complete the mixture was refluxed for 4 h. The Grignard complex was decomposed by pouring the mixture into ice–water containing some hydrochloric acid. The organic layer was washed subsequently with water, sodium hydrogencarbonate solution, and water. The solvent of the dried solution ($MgSO_4$) was evaporated and the residue chromatographed on silica gel [eluant light petroleum (b.p. 40—60°)–toluene (16 : 1), the desired hydrocarbon eluted first] and recrystallized from ethanol.

Procedures for Reactions with Dioxan–SO_3 *Complex.*—Two reaction procedures have been applied. (i) To [$^2H_8$]dioxan (2.5 ml) SO_3 (2 mmol) was added slowly at 17 °C. To the resulting heterogeneous mixture was then added under nitrogen the aromatic hydrocarbon (2 mmol). The resulting mixture was stirred and samples were taken after the desired time (which were filtered if heterogeneous) for ^1H n.m.r. analysis. (ii) To dioxan (10 ml) SO_3 (2 mmol) was added slowly at 17 °C. To the heterogeneous mixture was added under nitrogen the substrate (2 mmol) and the mixture stirred for 1 h. Then the mixture was poured into ice–water (50 ml) and any unconverted hydrocarbon (if present) filtered off. The filtrate was made just alkaline with 10% NaOH to pH 8, and the solvent removed by freeze-drying. The sulphonates were then extracted from the residue with [$^2H_6$]dimethyl sulphoxide. The composition of the resulting solutions was determined by ^1H n.m.r. spectroscopy.

^1H *N.M.R. Analysis.*—The spectra were recorded with a Varian HA-100 or XL-100 spectrometer; the chemical shifts (δ) are relative to external neat tetramethylsilane (capillary). NOE data were determined on dilute, deoxygenated samples in [$^2H_6$]dimethyl sulphoxide, as an average of repeated integrations of the signal in question with the external oscillator on and off resonance.

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* In the reaction of 9-(prop-1-enyl)anthracene with dioxan–SO_3 this sulphonic acid has been obtained after work-up as sodium 1-(9-anthryl)prop-1-ene-3-sulphonate.[5]

† 9-Neopentylanthracene was recently obtained in >80% yield by addition of neopentyl-lithium to anthrone, followed by dehydration during work-up.[19]

I.r. Analysis.—The spectra (KBr) were recorded with a Perkin-Elmer 177 spectrometer.

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REFERENCES

[1] Part 71, A. Koeberg-Telder, T. A. Kortekaas, and H. Cerfontain, *J.C.S. Perkin II*, 1979, 851.

[2] H. Cerfontain, A. Koeberg-Telder, C. Ris, and C. Schenk, *J.C.S. Perkin II*, 1975, 966.

[3] (*a*) J. Flood, A. D. Mosnaim, and D. C. Nonhebel, *Chem. Comm.*, 1970, 76; (*b*) H. Suzuki, H. Yoneda, T. Hanafusa, and T. Sugiyama, *Bull. Inst. Chem. Res.*, 1976, **54**, 176.

[4] H. Cerfontain, A. Koeberg-Telder, C. Kruk, and C. Ris, *Analyt. Chem.*, 1974, **46**, 72.

[5] F. van de Griendt and H. Cerfontain, *J.C.S. Perkin II*, 1980, 23.

[6] N. B. Colthup, *J. Optical Soc. Amer.*, 1950, **40**, 397.

[7] J. M. Mancilla, D. C. Nonhebel, and J. A. Russell, *Tetrahedron*, 1975, **31**, 3097.

[8] M. Herlem, A. Thiebault, and G. Adhami, *Analyt. Letters*, 1977, **10**, 67.

[9] F. van de Griendt and H. Cerfontain, *J.C.S. Perkin II*, submitted for publication.

[10] J. W. Larsen, P. A. Bouis, C. R. Watson, jun., and R. M. Pagni, *J. Amer. Chem. Soc.*, 1974, **96**, 2284.

[11] H. Cho, R. G. Harvey, and P. W. Rabideau, *J. Amer. Chem. Soc.*, 1975, **97**, 1140.

[12] H. V. Ansell, M. M. Hirschler, and R. Taylor, *J.C.S. Perkin II*, 1977, 353.

[13] E. E. Gilbert, 'Sulfonation and Related Reactions,' Interscience, New York, 1965, p. 31.

[14] A. Koeberg-Telder and H. Cerfontain, *Rec. Trav. chim.*, 1972, **91**, 22.

[15] P. H. Gore, *J. Org. Chem.*, 1957, **22**, 135; A. Koeberg-Telder and H. Cerfontain, unpublished results.

[16] F. van de Griendt and H. Cerfontain, following paper.

[17] F. van de Griendt and H. Cerfontain, *Tetrahedron Letters*, 1978, 3263.

[18] F. Krollpfeiffer and F. Brandscheid, *Ber.*, 1923, **56**, 1617; R. Lalande and R. Calas, *Bull. Soc. chim. France*, 1959, 766.

[19] M. Bullpitt and W. Kitching, *Synthesis*, 1977, 316.