Aromatic Sulphonation. Part XLIX.[1] Sulphonation of Anthracene and Some *meso*-Substituted Hydrocarbon Derivatives: Mechanism of Methyl Side-chain Sulphonation

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The sulphonation of anthracene and 9-phenyl-, 9-methyl-, and 9,10-dimethyl-anthracene with dioxan–SO_3 in dioxan has been studied at 40°. With all substrates substitution products and no addition products are formed. With the first two substrates sulphonation occurs predominantly at the *meso*-position, the substitution distribution being 66 ± 8 9-, 26 ± 3 1-, and 8 ± 2% 2-substitution with anthracene, and 67 ± 4 10- and 33 ± 4% 4-substitution with 9-phenylanthracene. With the *meso*-methylated anthracenes not ring but methyl substitution takes place, the only products being 9-anthrylmethanesulphonic acid with 9-methylanthracene, and 10-methyl-9-anthrylmethanesulphonic acid and 9,10-bis-sulphomethylanthracene with 9,10-dimethylanthracene. It is proposed that the methyl sulphonation occurs by initial addition of SO_3 to the opposite *meso*-position and subsequent loss of SO_3 from the methyl sulphonated σ-complex. A similar but more complex mechanism is proposed to explain the methyl sulphonation of 7-isopropyl-1,4-dimethylazulene.

As part of our studies on kinetic isotope effects in electrophilic aromatic substitution,[2] we recently reported that the sulphonation of anthracene with dioxan–SO_3 at the 9-position proceeds with a maximal substrate kinetic isotope effect.[3] At that time it was already known that aprotic sulphonation with dioxan–SO_3 proceeds predominantly at the 9-position,[4] whereas protic sulphonation with chlorosulphuric acid, or 95% H_2SO_4, yields only anthracene-1- and -2-sulphonic acids.[5]

In order to obtain more information on the mechanism of the reaction, we have studied the sulphonation of anthracene and some *meso*-substituted anthracene derivatives.

RESULTS

Anthracene.—Anthracene was sulphonated with dioxan–SO_3 in dioxan. Unchanged anthracene was removed and the sulphonic acids were converted quantitatively into their sodium salts. The isomeric composition of the sodium sulphonates was determined by multicomponent ^1H n.m.r. analysis.[6] The 1,5- and 1,8-disulphonates are absent.[3] The results are in Table 1. The maximum anthracene conversion is 90%. The isomer ratios are independent of the substrate conversion. Prolonged reaction times do not alter these ratios. Accordingly, the reported isomer ratios are kinetically controlled.

TABLE 1

Sulphonation of anthracene (12.3 mmol) with dioxan–SO_3 (14 mmol) in dioxan (10 ml)

Substrate	Time (h)	Temp. (°C)	Unconverted anthracene (%)	9-$ArSO_3Na$ / 1-$ArSO_3Na$	2-$ArSO_3Na$ / 1-$ArSO_3Na$
Anthracene	1.0	13	>99		
	20.0	13	92	2.5 ± 0.3	
	1.0	13—40	36	2.5 ± 0.2	
	4.0	13—40	10	2.8 ± 0.3	
	20.0	13—40	9	2.6 ± 0.3	0.33 ± 0.10
[9-^2H]-Anthracene	20.0	13—40	11	*a*	0.27 ± 0.09[3]

[a] With [9-^2H]anthracene, $k_{10}/k_1 = 6.9 \pm 1.2$, [3] *i.e.* equal within experimental error to the k_9/k_1 ratio (5.2 ± 0.6) of unlabelled anthracene.

In order to test whether interconversion of the acids occurs,† anhydrous anthracene-1-sulphonic acid (5.3 mmol) was treated with dioxan–SO_3 (1.8 mmol) in dioxan (4 ml) at 40° for 4 h. N.m.r. analysis of the sodium sulphonates obtained on work-up showed the presence of only the 1-sulphonate, the limits of detection of the 9-sulphonate and the 1,5- and 1,8-disulphonates being 0.2, 0.5, and 0.5% respectively. Thus no isomerization and sulphonation of the 1-sulphonic acid takes place. Anthracene was further sulphonated with acetylsulphuric acid in acetic anhydride at 0° for 2.5 h. The insoluble residue consisted only of anthracene. The filtrate contained the 9- and 1-sulphonic acids in the ratio of 2.6 ± 0.5. In this more protic sulphonation medium slow isomerization of the 9- into the 1-sulphonic acid was observed, the 9-: 1- ratio after 50 h at room temperature being only 1.2 ± 0.2.

9-Phenylanthracene.—Sulphonation of this compound with dioxan–SO_3 in dioxan at 40° for 18 h yields 34 ± 4% unconverted substrate, 34 ± 2% 9-phenyl-10-, and 17 ± 2% 9-phenylanthracene-4-sulphonic acid. In addition, a product was formed (*ca.* 15%) which results from addition of dioxan–SO_3 to 9-phenylanthracene at the 10-position, δ 7.9—8.4 (2H), 7.2—7.8 (11H), and 3.5—3.9 (<14 H): in all likelyhood this is $ArCH_2CH_2OCH_2CH_2OSO_3Na$.

In order to test whether the sulphonated products obtained in sulphonation of anthracene and 9-phenylanthracene with dioxan–SO_3 in dioxan are already formed from the σ-complex intermediate during sulphonation, or whether they are formed upon quenching the reaction mixture with water, the sulphonation reactions were carried out under similar conditions using [$^2H_8$]dioxan. After 4 h of reaction at 40°, the heterogeneous reaction mixtures were left for 30 min to let the insoluble material precipitate. The ^1H

† This would infer that the kinetically and thermodynamically controlled isomer ratios are the same.

[1] Part XLVIII, A. Koeberg-Telder and H. Cerfontain, *Tetrahedron Letters*, 1974, 3535.

[2] H. Cerfontain and A. Telder, *Rec. Trav. chim.*, 1967, **86**, 371; C. W. F. Kort and H. Cerfontain, *ibid.*, 1967, **86**, 865; J. K. Bosscher and H. Cerfontain, *J. Chem. Soc.* (*B*), 1968, 1524; M. P. van Albada and H. Cerfontain, *Rec. Trav. chim.*, 1972, **91**, 499; C. Ris, Thesis (in English), University of Amsterdam, 1973, p. 29.

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

[4] H. Zorn, O. Hinterhofen, and H. Schindlbauer, *Monatsh.*, 1967, **98**, 2406.

[5] M. Battegay and P. Brandt, *Bull. Soc. chim. France*, 1922, **31**, 910; 1923, **33**, 1667.

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

n.m.r. spectra of the resulting clear supernatant solutions did not exhibit any absorption at δ 3.8—7.0 illustrating the absence of the $CHSO_3^-$, $CHS_2O_6^-$ (or possbily $CHSO_3H$),* and the $CH(O^+C_4D_8O)$ groups. With anthracene as substrate, the [$^2H_8$]dioxan spectrum showed specific absorptions (*cf.* ref. 3) of the 9-sulphonic acid, δ 9.45 (d, *J* 9 Hz, 1- and 8-H) and 8.89 (s, 10-H), and the 2-isomer, δ 7.88 (dd, *J* 1.6 and 7 Hz). With 9-phenylanthracene specific absorptions of the 10-sulphonic acid, δ 9.56 (d, *J* 9 Hz, 4- and 5-H), the 4-sulphonic acid, δ 9.56 (s, 10-H), 8.47 (d, *J* 7 Hz), and 8.37 (d, 7 Hz, 3- and 5-H), and unconverted substrate, δ 8.62 (s, 10-H) and 8.14 (dd, *J* 1.8 and 8 Hz, 4- and 5-H), were apparent.

9-*Methylanthracene*.—Sulphonation of this compound with dioxan–SO_3 in dioxan at 40° for 18 h yields 23% unconverted substrate and 77% of a single sodium sulphonate which on the basis of the elemental analysis and ^1H and ^{13}C n.m.r. spectra was shown to be sodium 9-anthrylmethanesulphonate (see Experimental section).

9-Methylanthracene was also sulphonated in [$^2H_8$]dioxan for 20 min at 40°. The ^1H n.m.r. spectrum of the clear supernatant [$^2H_8$]dioxan solution revealed the specific absorptions of only 9-methylanthracene, δ 8.47 (s, 10-H), 8.42 (d, *J* 7 Hz, 1- and 8-H), 8.15 (dd, *J* 7 and 2 Hz, 4- and 5-H), and 7.90—7.50 (m, 2-, 3-, 6-, and 7-H), and 9-anthrylmethanesulphonic acid, δ 8.69 (s, 10-H), 8.63 (d, *J* 7 Hz, 1- and 8-H), 8.15 (dd, *J* 7 and 2 Hz, 4- and 5-H), and 7.90—7.50 (m, 2-, 3-, 6-, and 7-H).

9 10-*Dimethylanthracene*.—Sulphonation of this hydrocarbon with dioxan–SO_3 yields a mixture of 88% 10-methyl-9-anthrylmethanesulphonic acid and 12% of 9,10-bis-sulphomethylanthracene.

During dioxan–SO_3 sulphonations, dioxan decomposition products were formed, especially with substrates of low reactivity towards sulphonation as is apparent from the characteristic ^1H n.m.r. absorptions at δ 3.4—3.6. For reaction with 1.2 equiv of dioxan–SO_3, the amount of dioxan decomposition products increases in the order 9-methylanthracene (where these products are not formed) < anthracene < 9,10-dimethylanthracene < 9-phenylanthracene ≪ naphthalene, *i.e.* in the order of decreasing sulphonation reactivity.

Reaction of 9,10-dimethylanthracene with acetylsulphuric acid in acetic anhydride at 95° [5b] did not lead to sulphonation of the methyl side chains as the sulphonated product in dimethyl sulphoxide exhibited no absorption in the δ 4.0—6.0 region, but only one methyl singlet at δ 3.0.

DISCUSSION

The observed sulphonation reactivity order of anthracene (9 > 1 > 2) agrees with that predicted on the basis of localization energies.[8] That of 9-phenylanthracene (10 > 4 > 1,2,3,4′) is determined by localization energies and steric hindrance. The dihedral angle of 67° between the planes of the phenyl and anthryl groups [9] makes internal conjugation rather limited. Based on electronic effects, the reactivity order of 9-phenylanthracene will thus be *meso* > α > β ⋙ 4′. Further, because of steric hindrance by the phenyl group, substitution at positions 1 and 8 will be strongly inhibited.

The absence of the 9-sulphonic acid as a product in the protic sulphonation of anthracene with chlorosulphuric acid and 95% H_2SO_4 deserves some comment. It has been explained in three ways, (i) in terms of the 9-anthrylium ion being the actual and *only* species undergoing sulphonation,[10] (ii) in terms of steric hindrance by the adjacent α-hydrogens,[11] and (iii) in terms of rapid isomerization of the initially formed 9-sulphonic acid.[10,12] The first explanation presumes that anthracene would be converted completely into the 9-anthrylium ion. Based on a pK_a value for this ion of −7.8,[13] the [ArH_2^+]/[ArH] ratio in 95% H_2SO_4 will be 12. The reactivity of anthracene will, however, be at least 10^4 times that of the conjugated acid, thus rendering the first explanation very unlikely. The second explanation is unattractive in view of the formation of the 9-sulphonic acid under aprotic sulphonation conditions.† This leaves the third explanation. The observed slow isomerization of the 9-sulphonic acid in the acetylsulphuric acid–acetic anhydride system is in line with this conclusion.

The ^1H n.m.r. experiments on the sulphonation of anthracene in [$^2H_8$]dioxan unequivocally showed that the sulphonic acid products are formed during sulphonation and that there is no evidence at all for the presence of detectable amounts of a σ-complex or a 9,10-sulphur trioxide–dioxan addition complex of anthracene. The formation of the sulphonic acids of anthracene is thus expected to proceed by the mechanism proposed [15] for the sulphur trioxide complexing solvents (B), *viz.* by sequence (1)—(3), but for which step (3) is now rate limiting.[3]

$$ArH + B,SO_3 \rightleftharpoons Ar^+(SO_3^-)H + B \quad (1)$$

$$Ar^+(SO_3^-)H + B,SO_3 \rightleftharpoons Ar^+(SO_2{\cdot}OSO_3^-)H + B \quad (2)$$

$$Ar^+(SO_2{\cdot}OSO_3^-)H \longrightarrow ArS_2O_6H \quad (3)$$

* Based on a comparison of the chemical shifts of CH_3SO_3H (3.83) and $C_6H_5CH_2SO_3H$ (5.12) on the one hand, and of the corresponding anions on the other (*viz.* δ 3.30 and 4.73 respectively),[7] it is to be expected that the chemical shifts of the $CHSO_3H$ and $CHSO_3^-$ systems in the anthracene σ-complexes or the anthracene addition complexes will be at δ 5.8—6.7.

† The steric hindrance for the sulphonation with SO_3 and 95% H_2SO_4 as reagent is the same, as judged from the differences in activation entropy for the *para*- and *ortho*-substitution of toluene (4.7 ± 1.4 and 4.8 ± 0.7 cal K^{-1} mol^{-1} respectively.)[14]

[7] A. Koeberg-Telder and H. Cerfontain, *J.C.S. Perkin II*, 1975, 226.

[8] A. Streitwieser, 'Molecular Orbital Theory for Organic Chemists,' Wiley, New York, 1961, ch. 11.

[9] E. D. Bergmann, M. Rabinovitz, M. J. Aroney, R. J. W. Le Fèvre, L. Radom, and G. L. D. Ritchie, *J. Chem. Soc.* (*B*), 1968, 1551.

[10] H. Cerfontain, 'Mechanistic Aspects in Aromatic Sulphonation and Desulphonation,' Interscience, New York, 1968, p. 73.

[11] G. M. Badger, 'The Structures and Reactions of Aromatic Compounds,' Cambridge University Press, Cambridge, 1954, p. 305.

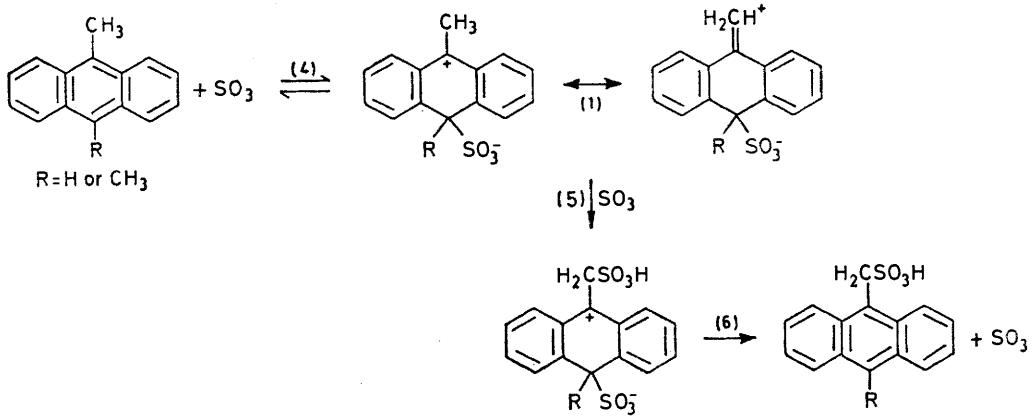
[12] P. H. Gore, *J. Org. Chem.*, 1957, **22**, 135.

[13] T. Handa, *Yoki Gosei Kagaku Kyokai Shi*, 1956, **14**, 550 (*Chem. Abs.*, 1956, **51**, 8439).

[14] H. Cerfontain, A. Telder, and L. Vollbracht, *Rec. Trav. chim.*, 1964, **83**, 1103.

[15] J. A. Walsh and D. A. Davenport, *Diss. Abs.*, 1964, **24**, 5013; J. K. Bosscher and H. Cerfontain, *Rec. Trav. chim.*, 1968, **87**, 873.

The side chain sulphonation of 9-methyl- and 9,10-dimethyl-anthracene may be explained by the mechanism outlined in Scheme 1. It is presumed that the transfer of sulphur trioxide from dioxan–SO_3 to the *meso*-position of the methylanthracenes [step (4)] is fast relative to direct electrophilic sulphonation at the methyl group.* With 9-methylanthracene this transfer will occur predominantly to the 10-position because of hyperconjugative stabilization by the methyl group. This hyperconjugation enhances the acidity of the hydrogens of the methyl group at position 9 and renders them more susceptible towards electrophilic sulphonation [step (5)]. This sulphonation probably proceeds by initial proton loss and subsequent sulphur trioxide addition. Because of the electron-withdrawing effect of the sulphomethyl substituent, the resulting σ-complex will lose sulphur trioxide with formation of the observed reaction product [step (6)]. The alternative, *i.e.* loss of the proton, does not occur. In fact, this proton-removing step will be relatively very slow because of inhibition as a result of steric hindrance between the incoming sulphonate group and the two *peri*-hydrogens, as was observed in the formation of anthracene-9-sulphonic acid.[2] The ^1H n.m.r. [$^2H_8$]dioxan experiments revealed that the concentration of the σ-complexes is undetectably low. As judged from the amounts of dioxan decomposition products (see Results section), the sulphonation of 9-methylanthracene is faster than that of anthracene. This infers that the loss of the proton from C-10 in (1; R = H), possibly after an initial SO_3 addition to the sulphonate group,[15] is slow compared with methyl sulphonation of (1; R = H).



SCHEME 1

Side-chain sulphonation was also observed with methanesulphonic acid,[17a] 2-phenylindane-1,3-dione,[18] 7-isopropyl-1,4-dimethylazulene,[19] and with 1,5-dimethylnaphthalene,[20] the products being methanedisulphonic acid, 2-phenyl-1,3-dioxoindane-2-sulphonic acid, 7-isopropyl-4-methyl-1-sulphomethylazulene, and probably 5-methyl-1-sulphomethylnaphthalene-6-sulphonic acid, respectively. So far, no attempts have been made to explain the mechanism of the side-chain sulphonation. For the latter compound, side-chain sulphonation may be explained along similar lines to those proposed for 9-methylanthracene. With the former two compounds the hydrogens to be substituted are weakly acidic because of the electron-withdrawing effects of the adjacent sulpho- and carbonyl groups respectively, and they are thus apt to undergo direct electrophilic sulphonation.† The methyl hydrogens in 7-isopropyl-1,4-dimethylazulene, however, will be less acidic than those in *e.g.* toluene, *i.e.* not acidic enough to undergo sulphonation. In the sulphonation of 7-isopropyl-1,4-dimethylazulene with fuming sulphuric acid, the additional product is the 2-sulphonic acid.[19] The formation of the two sulphonation products may be explained (Scheme 2) to proceed *via* the common intermediate (3.) The initial step is the complete protonation of 7-isopropyl-1,4-dimethylazulene at position 3 [21] [step (7)]. Transfer of SO_3H^+ from the solvent [22] to the resulting vinyltropylium ion (2) yields the dication (3). The 1-methyl hydrogens of (3) are weakly acidic and labile to electrophilic sulphonation which is proposed to proceed *via* intermediate (4) by initial proton loss [step (9)] and subsequent sulpho-addition [step (10)]. Because of the electron-withdrawing effect of the sulphomethyl group, the disulphonic acid entity (5) is apt to lose H^+ or SO_3H^+ from C-2. The leav-

* For example, no methyl sulphonation is observed on reaction of toluene or its anhydrous *o*- and *p*-sulphonic acids with SO_3.[16]

† The non-acidic hydrogens of the aliphatic hydrocarbons are, for example, very difficult to sulphonate.[17b]

[16] A. Koeberg-Telder and H. Cerfontain, *Rec. Trav. chim.*, 1971, **90**, 193.

[17] E. E. Gilbert, 'Sulfonation and Related Reactions,' Interscience, New York, 1965 (*a*) p. 41; (*b*) p. 31.

[18] A. Y. Strakov, E. Y. Gudriniece, A. F. Ievins, and G. Y. Vanags, *J. Gen. Chem. U.S.S.R.*, 1960, **30**, 3925.

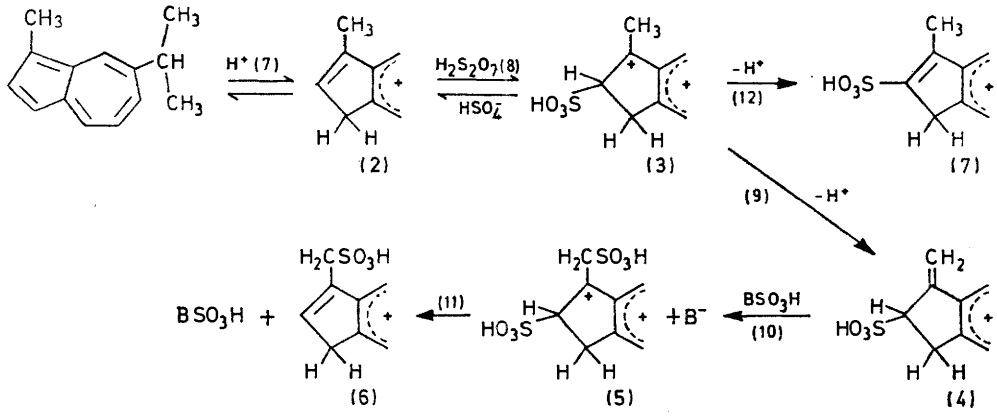
[19] W. Meier, D. Meuche, and E. Heilbronner, *Helv. Chim. Acta*, 1963, **46**, 1929.

[20] Z. R. H. Schaasberg-Nienhuis and H. Cerfontain, preliminary results.

[21] J. Schulze and F. A. Long, *J. Amer. Chem. Soc.*, 1964, **86**, 322.

[22] C. W. F. Kort and H. Cerfontain, *Rec. Trav. chim.*, 1969, **88**, 1299.

ing ability will be greater for SO_3H^+ than for H^+,* in part as result of the steric hindrance that would arise between the adjacent sulphomethyl and sulpho-groups upon proton removal from C-2, as the latter group then has to enter the plane of the 7-isopropyl-1,4-dimethyl-azulene molecule. Loss of SO_3H^+ from (5) yields the protonated sulphomethylated product (6). Finally the formation of 7-isopropyl-1,4-dimethylazulene-2-sulphonic acid may be explained by proton loss from the dication (3) [step (12)] yielding the protonated acid (7).



SCHEME 2

TABLE 2

^1H N.m.r. data of anthracene and derivatives

Substituents	Solvent	δ 1-	2-	3-	4-	5-	9-	10-	benzylic-H
	[$^2H_6$]DMSO	8.09(m)	7.52(m)				8.57(s)		
1-SO_3Na	[$^2H_6$]DMSO		8.0—8.2(m)	7.4—7.6(m)	—8.0—8.2(m)—		9.52(s)	8.57(s)	
1-SO_3Na	Acetylsulphuric acid		7.6—8.2(m)		—7.6—8.2(m)—		8.85(s)	8.30(s)	
1-SO_3Na	D_2O		7.6—7.9(m)		—7.6—7.9(m)—		9.15(s)	8.05(m)	
2-SO_3Na	[$^2H_6$]DMSO	8.33(s)		7.72(d,d [a])	—8.0—8.2(m)—		8.63(s)	8.54(s)	
9-SO_3Na	[$^2H_6$]DMSO	9.67(m)	—7.4—7.6(m)—		—7.9—8.1(m) —			8.59(s)	
9-SO_3Na	Acetylsulphuric acid	8.85(d)	—7.2—7.5(m)—		—7.8—8.0(d)—			8.65(s)	
9-Ph	[$^2H_6$]DMSO	—7.3—7.7(m)—			—8.14(m)—			8.66(s)	
9-Ph-2-SO_3Na	[$^2H_6$]DMSO	7.6—8.0 [b]		7.5—7.9 [b]	—8.14 [b] —			8.66 [b]	
9-Ph-3-SO_3Na	[$^2H_6$]DMSO	7.3—7.7 [b]	7.5—7.9 [b]		8.41 [b]	8.14 [b]		8.75 [b]	
9-Ph-4-SO_3Na	[$^2H_6$]DMSO	—7.2—7.7(m)—		7.9—8.2(m)		7.9—8.2(m)		9.61(s)	
		—7.3—7.7 [b] —		7.8—8.1 [b]		8.14 [b]		9.61 [b]	
9-Ph-10-SO_3Na	[$^2H_6$]DMSO	—7.2—7.7(m)—			9.78 (m)				
		—7.3—7.7 [b] —			9.73 [b]				
9-Me	[$^2H_6$]DMSO	8.32(m)	7.53(m)		8.05(m)			8.44(s)	3.03(s)
9-Me-10-SO_3Na	[$^2H_6$]DMSO				9.64 [b]				3.03 [b]
9-Me-4-SO_3Na	[$^2H_6$]DMSO							9.39 [b]	3.03 [b]
9-CH_2SO_3Na	[$^2H_6$]DMSO	8.47(m)	—7.43—7.55(m)—		7.99(m)			8.44(s)	4.88(s)
9-CH_2SO_3Na	D_2O	8.03(d,d) [a]	—7.1—7.5(m)—		7.51(d)			7.77(s)	4.82(s)
9,10-Me_2	[$^2H_6$]DMSO	8.37(m)	7.55(m)						3.05(s)
9-CH_2SO_3Na-10-Me	[$^2H_6$]DMSO	8.55(m)	— 7.52(m) —		8.32(m)				3.03(s)
									5.00(s)
		8.52 [b]	— 7.55 [b] —		8.37 [b]				3.05; [b]
									4.90 [b]
9,10-(CH_2SO_3Na)$_2$	[$^2H_6$]DMSO	8.55(m)	7.52(m)						5.05(s)

[a] $J_{1,2}$ 8—9, $J_{1,3}$ 1—2 Hz. [b] Chemical shifts calculated on the basis of additivity of substituent effects.

The structures of the protonated species (6) and (7) have been established.[19] The observation that both the methyl- and 2-sulphonation of 7-isopropyl-1,4-dimethyl-azulene occur only with the highly acidic fuming sulphuric acid reagent, and not with the less protic acetyl-sulphuric acid reagent (which yields 7-isopropyl-1,4-dimethylazulene-3-sulphonic acid [19]), illustrates that the former two sulphonations proceed *via* intermediate (2).

Further, it seems of interest that methyl nitration has been observed with toluene,[24] 1,4-dimethylnaphthalene,[25]

* The leaving ability from the σ-complex intermediates in electrophilic aromatic substitution is reported to be somewhat greater for SO_3 than for H^+.[23]

[23] C. L. Perrin, *J. Org. Chem.*, 1971, **36**, 420.

[24] S. R. Hartshorn, R. B. Moodie, and K. Schofield, *J. Chem. Soc.* (*B*), 1971, 1256.

[25] R. Robinson and H. W. Thompson, *J. Chem. Soc.*, 1932, 2015; A. Fischer and A. L. Wilkinson, *Canad. J. Chem.*, 1972, **50**, 3988.

and hexamethylbenzene,[26] and methyl halogenation with C_6Me_5X (X = Me, Cl, or CN).[27]

EXPERIMENTAL

The aromatic hydrocarbons were commercial high purity products. The preparation of the three sodium anthracenesulphonates has been described.[3] Anhydrous anthracene-1-sulphonic acid was obtained by pouring a dilute aqueous solution of sodium anthracene-1-sulphonate over a Dowex 50W-X8 cation exchange column, followed by removal of the water by distillation and subsequent drying *in vacuo* over P_2O_5.

Sulphonation Procedures.—(a) To dioxan (10 ml), SO_3 (14 mmol) was added slowly at 11—14°. To the heterogeneous mixture was then added in portions at 12° under nitrogen a total of 12 mmol of the aromatic hydrocarbon. The resulting mixture was kept stirred for the desired time, if not specified, 20 h, at 40°. After cooling, water (25 ml) was added drop by drop at 10°. Unconverted hydrocarbon was filtered off. The filtrate was made just alkaline with 10% NaOH to pH 8. The solvent was removed and the residue containing the sulphonates dried *in vacuo* at 40°.

(b) To acetic anhydride (40 mmol) was added cautiously anthracene (10 mmol). Then with ice cooling, 98% H_2SO_4 (60 mmol) was added and the mixture left for 2.5 h. Filtration of the reaction mixture yielded unchanged anthracene. The filtrate was analysed by ^1H n.m.r. spectroscopy.

N.m.r. Isomer Analysis.—The sodium sulphonates obtained from dioxan–SO_3 sulphonations were dissolved in [$^2H_6$]dimethyl sulphoxide. The composition of these solutions, as well as the sulphonic acid solutions in acetic anhydride obtained from acetylsulphuric acid sulphonations were determined by ^1H n.m.r. multicomponent analysis.[6] The identification of the three anthracenesulphonates was made by comparison with authentic samples.[3] The assignment of the sulphonates of 9-phenylanthracene was based on the occurrence of the low field absorptions which coincide with the absorptions calculated for these sulphonic acids on the basis of additivity of the sulphonic acid substituent effect, as determined from the anthracene–anthracenesulphonic acids series (Table 2). The n.m.r. spectrum does not exhibit an absorption at δ 8.25—9.5, illustrating the absence of the 9-phenylanthracene-β-sulphonates at the limits of detection, *i.e.* 4%.

Sulphonation of 9-methylanthracene leads to the formation of one single product (Found: C, 61.1; H, 4.0; Na, 7.7; S, 10.9. Calc. for $C_{15}H_{11}NaSO_3$: C, 61.2; H, 3.8; Na, 7.8; S, 10.9%), δ 8.47 (2H, m), 7.99 (2H, m), 7.43—7.55 (4H, m), and 4.88 (2H, s). The product is considered to be sodium 9-anthrylmethanesulphonate (*cf.* Table 2). The absence of absorptions in the δ 2.8—3.3 region excludes the ring substituted sulphonate structures. The presence of the methylene group was further proven by the occurrence of a triplet absorption (with J 60 Hz) in the off resonance ^{13}C n.m.r. spectrum of the sulphonate in [$^2H_6$]dimethyl sulphoxide as solvent.

With most substrates the sodium sulphonate residues also contain (a) dioxan decomposition product(s) with a characteristic absorption at δ 3.4—3.6.

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[26] H. Suzuki, *Bull. Chem. Soc. Japan*, 1970, **43**, 879; A. Astolfi, E. Baciocchi, and G. Illuminati, *Chimia e Industria*, 1971, **53**, 1153.

[27] E. Baciocchi and G. Illuminati, *Ricerca Sci.*, 1964, **34**, 462; E. Baciocchi, A. Ciana, G. Illuminati, and C. Pasini, *J. Amer. Chem. Soc.*, 1965, **87**, 3953; R. M. Keefer and L. J. Andrews, *J. Org. Chem.*, 1966, **31**, 541.