Aromatic Sulphonation. Part 78.[1] Behaviour of Some α-Chloro-substituted 9-Methyl-, 9-Ethyl-, 9-Isopropyl-anthracenes, and of 1,4,9-Trimethylanthracene in Dioxan–Sulphur Trioxide Complex in Dioxan as Sulphonating Medium

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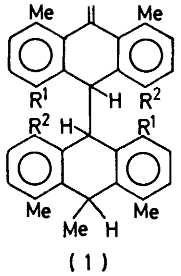
The reaction of some α-chloro-substituted 9-methyl-, 9-ethyl-, 9-isopropyl-anthracenes and of 1,4,9-trimethylanthracene (3a—j), with dioxan–SO_3 in dioxan has been studied at 25 °C. All the methylanthracene derivatives (3a—d) yield α-sulphonic acids (4a—d). 1,5-Dichloro-9-methyl- and 1,4,9-trimethyl-anthracene yield, in addition, the dimer (5c) and the sultones (6l and m) respectively.

1-Chloro- and 1,5-dichloro-9-ethylanthracene yield the dimers (5e) and (5f) respectively. 4-Chloro-9-ethylanthracene yields the two sulphonic acids (4g) and (7g). 4,5-Dichloro-9-ethylanthracene does not react. 1-Chloro- and 1,5-dichloro-9-isopropylanthracene yield besides the dimeric products (5) and the sulphonic acids (9), products corresponding with those obtained in the sulphonation of 9-isopropylanthracene [*viz.* sultones (8), 9-allylanthracene derivatives (10), and the sulphonic acids (11) and (12)]. A mechanism for the formation of the products is presented. It is proposed that the dimeric products (5) and the sultone (6d) result from initial attack of SO_3 at C-9 and C-1 respectively, whereas all other products result from attack of SO_3 at C-10. The behaviour of the substrates (3a—j) in the sulphonation is compared with that in their protonation.

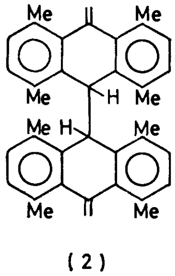
9-ALKYLIDENE-9,10-DIHYDROANTHRACENE derivatives are generally unstable relative to their tautomeric 9-alkylanthracenes. However in crowded systems in which the anthracene tautomer is highly energetic as result of steric strain 9-alkylidene-9,10-dihydroanthracene derivatives were isolated.[2]

Harvey *et al.*[2a] investigated the tautomeric equilibrium between 10-alkyl-9-isopropylidene-9,10-dihydroanthracenes and 10-alkyl-9-isopropylanthracene. The position of this equilibrium was shown to depend on the size of the alkyl group and, for example, 10-isopropyl-9-isopropylidene-9,10-dihydroanthracene was ' shown to be stable with respect to 9,10-di-isopropylanthracene '. This is the only reported example of a 9-alkylanthracene not substituted in the 1,4,5 and/or 8 position(s) in which the 9,10-dihydroanthracene form is the more stable isomer. Dickerman *et al.*[2b] reported that the catalytic hydrogenation of 9,10-dimethyl-1,4,5,8-tetraphenyl-9,10-dihydroanthracene yields both 10-methyl-9-methylene-1,4,5,8-tetraphenyl-9,10-dihydroanthracene and 9,10-dimethyl-1,4,5,8-tetraphenylanthracene. Cameron *et al.*[2c] reported the synthesis of a series of 9-methylanthracenes, and observed that (i) those systems which incorporated at most one *peri* methyl–methyl interaction, yield exclusively the anthracene tautomers as products, and (ii) those systems which in the anthracene tautomer would incorporate at least two *peri* methyl–methyl interactions and in which the crowding in the ' hypothetical ' anthracene tautomer could be relieved by a methyl-substituted C-9 or C-10 becoming tetrahedral yield the methylenedihydroanthracenes as products. They further observed that 1,8,9-trimethyl- and 1,4,8,9-tetramethyl-anthracene were obtained as anthracene tautomers (they cannot form stable methylenedihydroanthracenes in view of the absence of a 10-methyl group!), but that on treatment of these anthracenes with toluene-*p*-sulphonic acid they were converted into dimers (1) ($R^1 = R^2 = H$ and $R^1 = Me$, $R^2 = H$ respectively)

Hart *et al.*[2d] reported that 1,4,5,8,9-pentamethylanthracene (i) upon treatment with acid (unspecified conditions) gave a mixture of the anthracene tautomer and its 9-methylene-9,10-dihydroanthracene derivative (ii) upon reaction with toluene-*p*-sulphonic acid does not dimerize to (1; $R^1 = R^2 = Me$), and (iii) on treatment with sulphuryl chloride and silica gel in hexane and hydrolytic work-up yields the dimer (2).



(1)



(2)

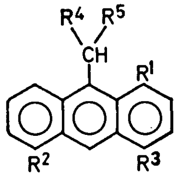
In our preceding papers on the sulphonation of 9-alkylanthracenes,[3] we suggested the intermediacy of 9-alkylidene-9,10-dihydroanthracene-10-sulphonic acid in the reaction of 9-alkylanthracenes leading to the corresponding 9-(alk-1-enyl)anthracenes. In view of the reports on stable 9-alkylidene-9,10-dihydroanthracenes we have now studied the 9-alkylanthracenes which are substituted at one or more α-position(s) by chlorine or methyl with the aim to obtain stable (and detectable) 9-alkylidene-9,10-dihydroanthracene-10-sulphonic acids. We were further interested to learn which type of dimer if any would result on reaction of our substrates with dioxan–SO_3.

RESULTS AND DISCUSSION

Product Formation.—The substituted 9-alkylanthracenes have been treated with [$^2H_8$]dioxan–SO_3 complex in [$^2H_8$]dioxan at 25 °C. Assignment of structure to the products obtained and determination of the composition of the reaction mixture was carried out by ^1H n.m.r.

analysis. Assignment of structure to the reaction products was in some cases supported by the evidence of ^{13}C n.m.r., i.r., and mass spectral data.

Substituted 9-*Methylanthracenes*.—The four investigated substrates [1-chloro- (3a), 4,5-dichloro- (3b), 1,5-dichloro- (3c), and 1,4-dimethyl-9-methylanthracene (3d)] yield the corresponding 9-anthrylmethanesulphonic acids (4a—d). The ^1H n.m.r. data of these sulphonic acids are given in Table 1. The first two substrates yield these products exclusively, the rate of substrate conversion for (3b) being lower than that for (3a): (3a) is completely converted within 15 min, whereas the reaction mixture of (3b) after 45 min still contained 14 ± 2% of unconverted substrate. The side-chain hydrogens of (4a) exhibit at *ca.* 30 °C a broad multiplet (δ 7.1—6.0) but, at 60 °C, a singlet (δ 6.55), indicating restricted rotation around the C(9)–C(α) bond. The presence of the sulphonic acid group in (4a) has been established [4] from the i.r. absorptions (KBr) at 1 185(s), 1 045(m), and 725(m) cm^{-1} of the isolated sodium salt.



(3)

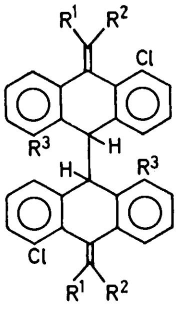
	R^1	R^2	R^3	R^4	R^5
a	Cl	H	H	H	H
b	H	Cl	Cl	H	H
c	Cl	Cl	H	H	H
d	Me	H	Me	H	H
e	Cl	H	H	Me	H
f	Cl	Cl	H	Me	H
g	H	H	Cl	Me	H
h	H	Cl	Cl	Me	H
i	Cl	H	H	Me	Me
j	Cl	Cl	H	Me	Me
k	H	H	H	Me	Me

(4)

	R^1	R^2	R^3	R^4	R^5
a	Cl	H	H	SO_3H	H
b	H	Cl	Cl	SO_3H	H
c	Cl	Cl	H	SO_3H	H
d	Me	H	Me	SO_3H	H
g	H	H	Cl	SO_3H	Me

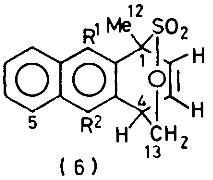
1,5-Dichloro-9-methylanthracene (3c) after 45 min of reaction gave 60 ± 10% of (4c), 25 ± 10% of the dimeric product (5c), besides 15 ± 10% of unconverted substrate. The assignment of (3b) is based on: (i) its ^1H n.m.r. absorptions (see Table 2), (ii) its i.r. absorptions (KBr) at 1 445 (s) and 785 (s) cm^{-1} [the same absorptions are observed with the dimeric products (5e) and (5f) obtained from 1-chloro- and 1,5-dichloro-8-ethylanthracene respectively], and (iii) its field ionization mass-spectral signals at *m/e* 518, 520, 522, and 524 in a ratio of *ca.* 8 : 11 : 5 : 1; the signal at 518 is in agreement with $^{12}C_{30}{}^{1}H_{18}{}^{35}Cl_4$ [≡(5c)], and the ratio of the observed signals is in agreement with that expected for the presence of four chlorine atoms.

1,4,9-Trimethylanthracene (3d), after 15 min of reaction yielded 67 ± 3% of (4d) and 33 ± 3% of the two sultones (6l and m) in a *ca.* 1 : 1 ratio. These sultones precipitated from the reaction mixture in 24 h. They were characterized by ^1H and ^{13}C n.m.r. spectroscopy. ^1H n.m.r. ($CDCl_3$): 8.0—7.3 (m, 5 H, ArH), 7.20 (br d, $J_{2,3}$ = 8 Hz, 1 H, 2-H), 6.92 (br d, $J_{2.3}$ = 8 Hz, 1 H, 3-H), 5.38 (m, 1 H, 4-H), 4.40 (m, 1 H, 13-H), 3.30 (m, 1 H, 13-H), 3.00 and 2.98 (two singlets, 3 H, 11-H), 2.61 and 2.54 (two singlets, 3 H, 12-H). ^{13}C N.m.r. ($CDCl_3$) for the aliphatic region: 56.4(C-1), 41.2 and 41.0(C-4), 29.1 and 28.1(C-13), 24.1 and 24.7(C-11), and 19.4 and 19.2(C-12); off resonance: a singlet for C-1, doublets for C-4, triplets for C-13, and quartets for the signals of C-11 and C-12. The high-field absorption of one of the C-13 hydrogens in the ^1H and of C-4 in the ^{13}C n.m.r. spectrum is most likely the result of shielding by the ' cyclohexadiene ' structure.



(5)

c; $R^1 = R^2 = H$; $R^3 = Cl$
e; $R^1 = R^3 = H$; $R^2 = Me$
f; $R^1 = H$; $R^2 = Me$; $R^3 = Cl$
i; $R^1 = R^2 = Me$; $R^3 = H$
j; $R^1 = R^2 = Me$; $R^3 = Cl$



(6)

l; $R^1 = Me^{11}$; $R_2 = H$
m; $R^1 = H$; $R_2 = Me^{11}$

Field ionization mass spectrometry gave a signal at

TABLE 1

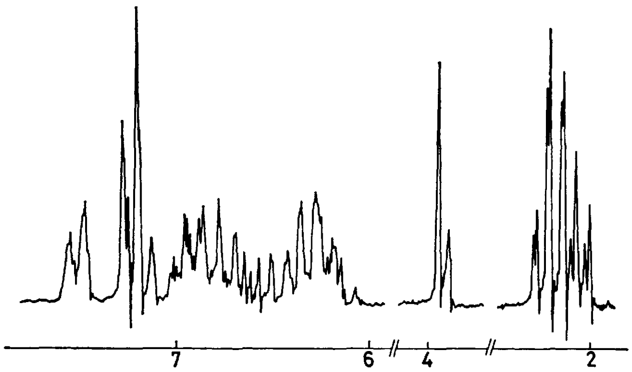
^1H N.m.r. data of the α-sulphonic acids in [$^2H_8$]dioxan [a]

	Chemical shifts δ and multiplicities (Hz)							
Compound	1-H	4-H	5-H	8-H	10-H	CH_2S	CHS	CH_3
(4a)		8.21 (m)	8.21 (m)	8.75 (d, J = 8)	8.79 (s)	6.55 (bs)		
(4b)		8.32 (d, J = 7)		8.72 (d, J = 9)	9.21 (s)	*ca.* 6.6 (bs)		
(4c)	8.61 (d, J = 9)			8.61 (d, J = 9)	9.55 (s)	5.75 (s)		
(4d)			8.26 (m)	8.70 (d, J = 9)	8.89 (s)	6.09 (bs)		
(4e)	8.66 (m)		*ca.* 8.2 (m)	9.04 (m)	9.21 (s)		6.35 (q, J = 8)	2.46 (d, J = 8)

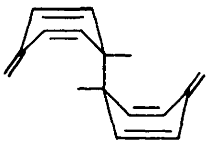
[a] The absorptions for the protons H(2,3,6,7) (if present) exhibit multiplets in the range 8.0—7.3 p.p.m.

m/e 210 which is in agreement with the molecular weight of (6d) minus 80 (loss of SO$_3$).

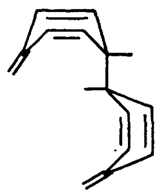
Substituted 9-*Ethylanthracenes*.—1-Chloro-(3e), 1,5-dichloro-(3f), 4-chloro-(3g), and 4,5-dichloro-9-ethylanthracene (3h) have been investigated. The first two substrates yield the dimeric products (5e) and (5f), which partially precipitated from the reaction mixtures. The reaction mixture of (3e) after 20 min contained no unconverted substrate but that of (3f) did, even after 45 min. The ^{1}H n.m.r. spectrum of (5e) in CDCl$_3$ is given in the Figure. The six doublet absorptions at *ca.* 2.2 ($J = 7$ Hz) have been ascribed to the methyl protons, the absorption at 3.9 to the methine protons, and the signals in the range 7.6—6.0 p.p.m. to the vinylic and aromatic protons. The assignment of the methyl and the vinylic protons have been supported by double-resonance experiments: on irradiation between 6.7 and 6.2 p.p.m. at different positions with intervals of 0.1 p.p.m. each doublet between 2.3 and 2.0 p.p.m. in turn becomes a singlet. The presence of at least six doublets at *ca.* 2.2 p.p.m. in the spectrum of (5e) can be explained on the basis of (i) the three possible stereoisomers of this dimer (*viz.* with the ' anthryl ' groups axial–axial, axial–equatorial, and equatorial–equatorial), and (ii) the possible *E*- and *Z*-configuration of both alkylidene double bonds. From the observation of two main doublets at 2.18 and 2.16 and the sharp singlet at 3.94 p.p.m. it appears that one stereoisomer is dominant.



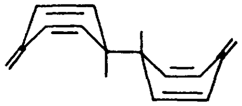
100 MHz ^{1}H n.m.r. spectrum of compound (5e)



axial - axial



axial - equatorial



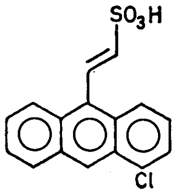
equatorial - equatorial

Based on its spectral similarity with *trans*, *trans*-10,10′-di-t-butyl-9,9′,10,10′-tetrahydro-9,9′-bianthracenyl,* this isomer exists in a twisted conformation in which one ring is in a plane *approximately vertical* with respect to the other (for a complete discussion on this subject and for the spectrum of this dimer, see ref. 5).

The assignment of (5e) was further supported by (i) field desorption mass spectrometry which showed signals at *m/e* 478 and 239 and electron impact mass spectrometry which showed a signal at *m/e* 239; the signal at 478 is in agreement with the molecular weight of (5e) and the signal at 239 results on breaking the C–C bond between both ' anthryl ' groups, (ii) the i.r. absorptions (CHCl$_3$) at 1 440 cm^{-1}, assigned to a threefold substituted C=C,[6] and (iii) an elemental analysis showed compound (5e) to be free of sulphur.

The product (5f) obtained from 1,5-dichloro-9-ethylanthracene after its precipitation from the reaction mixture could not be resolved. Its assignment is based on (i) its ^{1}H n.m.r. absorptions present in the spectrum of the reaction mixture before it started to precipitate (see Table 2), (ii) the i.r. (KBr) absorption at 1 445 cm^{-1}, and (iii) the electron impact mass spectral signals at *m/e* 546 and 273 which are in agreement with the molecular weight and half of it.

4-Chloro-9-ethylanthracene (3g) yields, as does 9-ethylanthracene,[3a] two sulphonic acids: after 95 min the reaction mixture of (3g) consisted of 50 ± 3% 1-(4-chloro-9-anthryl)ethane-1-sulphonic acid (4g), 12 ± 3% (*E*)-(4-chloro-9-anthryl)ethenesulphonic acid (7g), and 38 ± 3% unconverted substrate. Compound (7g) is only assigned on the basis of the ^{1}H n.m.r. absorption at 7.26 p.p.m. which is ascribed to H-C(β) (see Table 4 in which the corresponding sulphonic acid obtained from 9-ethylanthracene is included for comparison). 4,5-Dichloro-9-ethylanthracene (3h) gave no reaction with the applied sulphonating reagent even at 50 °C.



(7g)

Substituted 9-*Isopropylanthracenes*.—1-Chloro- (3i) and 1,5-dichloro-9-isopropylanthracene(3j) have been investigated. The reaction mixture of (3i) after 25 min contained 6 ± 3% of the dimeric product (5i), 23 ± 3% of the seven-membered ring sultone (8i), 27 ± 3% of the sulphonic acid (9i), 12 ± 3% (10i), 18 ± 3% of the (pyro)sulphonic acid † (11e), and 14 ± 3% (12i). The

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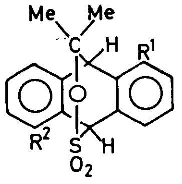
* This dimer, the structure of which was assigned tentatively, is obtained from 9-t-butyl-9,10-dihydroanthracene upon treatment with n-butyl-lithium–*N*,*N*,*N*′,*N*′-tetramethylethylenediamine complex, followed by treatment with cadmium(II) chloride.[5]

† For a discussion on the problem whether a sulphonic or a pyrosulphonic acid is formed, see ref. 3*c*.

reaction mixture of (3j) after 60 min contained besides 15 ± 3% unconverted substrate, 8 ± 3% (5j), 25 ± 3% (8j), 22 ± 3% (9j), 13 ± 3% (10j), 13 ± 3% (11j), and 4 ± 3% (12j). The dimeric products (5i) and (5j) have been assigned on the basis of their ^{1}H n.m.r. absorptions (Table 2) in relation to the observed absorptions for the dimers (5c), (5e), and (5f).



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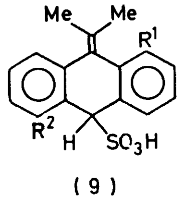

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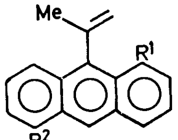

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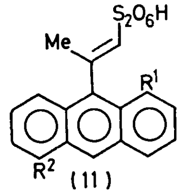

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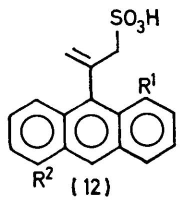


(12)

i; $R^1 = Cl; R^2 = H$
j; $R^1 = R^2 = Cl$
k; $R^1 = R^2 = H$

The seven-membered ring sultones (8i) and (8j) have been assigned on the basis of their ^{1}H n.m.r. absorptions (Table 3) and on a comparison of these absorptions with those of the seven-membered ring sultone (8k), obtained on sulphonation of 9-isopropylanthracene (3k). The two signals of (8j) at 1.53 and 1.59 p.p.m. are two singlets as appeared from a comparison of the 100 MHz with a 60 MHz ^{1}H n.m.r. spectrum. A *peri*-chloro-effect should be observed on 9-H and 10-H, if a *peri*-chlorine atom is present, since in this sultone both 9-H and 10-H are roughly in the plane defined by the four α-positions of the 'anthryl' group (for a discussion on this subject, see ref. 7). In fact, 9-H of (8i) and (8j) does absorb *ca.* 67 Hz at lower field than that of (8k) (which contains no chlorine atoms). Similarly for 10-H a chemical-shift difference of *ca.* 46 Hz is observed between (8j) on the one hand and (8i) and (8k) on the other.

The assignment of (9i) and (9j) is based on similar evidence to that described for the sultones (8i) and (8j), *viz.* the presence of two singlet absorptions for the methyl hydrogens at 2.18 and 2.07 p.p.m. and the observation of a *peri*-chloro-effect for 10-H in (9j). A *peri*-chloro-effect is to be expected, if 10-H is roughly in the plane defined by the four α-positions of the 'anthryl' group considering that the structures of (9i) and (9j) are similar to the structure established for 10-isopropyl-9-isopropylidene-9,10-dihydroanthracene.[2a]

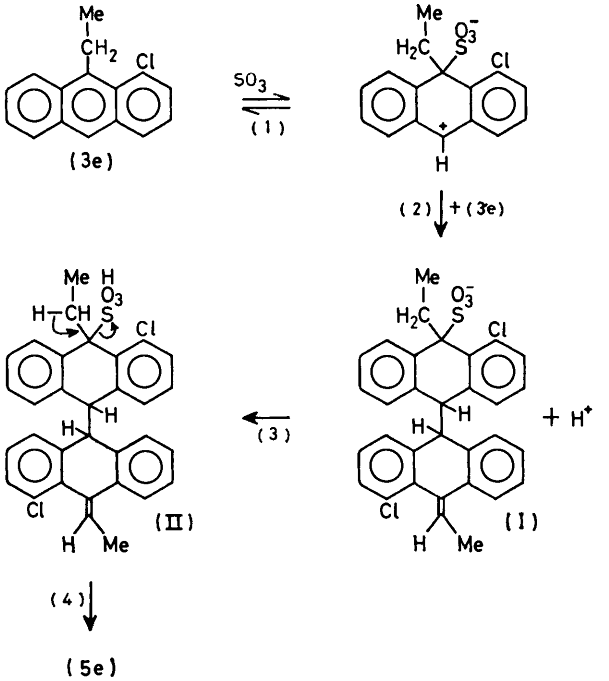
The structures of compounds (10)—(12) have been assigned tentatively by comparing their ^{1}H n.m.r. absorptions with those of the products obtained on reaction of 9-isopropylanthracene with dioxan–SO$_3$ [Table 4, the positions of 10-H in (10j), (11j), and (12j) are shifted *ca.* 45 Hz to lower field as result of a *peri*-chloro-effect].[8]

Mechanism of Product Formation.—The formation of the α-sulphonic acids from the substituted 9-alkylanthracenes (1)—(4) and (8) may be explained in terms of the mechanism already proposed for the unsubstituted 9-alkylanthracenes.[3a] This mechanism implies (i) initial electrophilic attack of SO$_3$ at C-10, leading to an enhanced acidity of the side-chain α-hydrogens which renders them more susceptible towards sulphonation, (ii) electrophilic sulphodeprotonation at the side-chain α-carbon, and (iii) loss of SO$_3$ from C-10 with formation of the products.

The unsaturated (pyro)sulphonic acids (7g), (11i), (12i), (11j), and (12j) (obtained from 4-chloro-9-ethyl-, 1-chloro-9-isopropyl-, and 1,5-dichloro-9-isopropyl-anthracene respectively) result from direct attack of SO$_3$ on the side-chain double-bond of 4-chloro-9-vinyl-, 9-allyl-1-chloro-(10i), and 9-allyl-1,5-dichloro-anthracene (10j) respectively. These unsaturated hydrocarbons are formed in a redox reaction between the 9-alkylanthracenes and SO$_3$ (for a more complete mechanistic discussion on this subject, see ref. 3*c*).

The seven-membered ring sultones (8i) and (8j) are [just like (8k) [3b]] formed by ring closure of the dipolar intermediate resulting from the σ-complex (formed by addition of SO$_3$ to the 10-position of 1-chloro- and 1,5-dichloro-9-isopropyl-anthracene respectively) by a 1,2-hydride shift from the side-chain C-α to C-9.

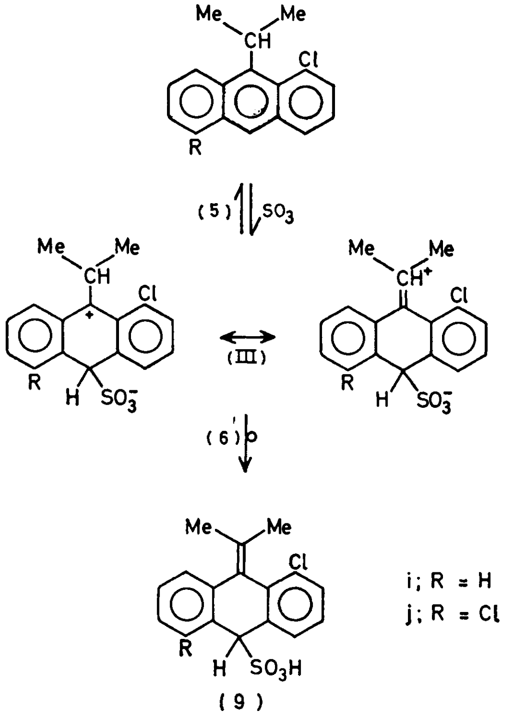
The mechanism of formation of the dimeric structure



SCHEME 1

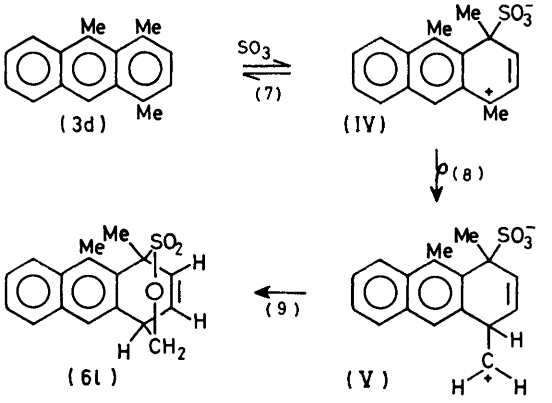
is formulated for 4-chloro-9-ethylanthracene in Scheme 1. The initial step is addition of SO_3 at C-9 [step (1)]. The resulting electrophile then reacts with another molecule of substrate, yielding the dimeric intermediate (I) [step (2)]. It is likely that the eventual redox reaction (4) is preceded by an inter- or intra-molecular proton shift [step (3)], as the concomitant electron transfer will be more difficult with (I) (where the electron is transferred towards the negative charge of the sulphonate group) than with (II). The formation of the sulphonic acids (11d) and (12d) obtained from 1-chloro- and 1,5-dichloro-9-isopropylanthracene proceeds (Scheme 2) by addition fo SO_3 to C-10 [step (5)] followed by a proton transfer from C-α to a sulphonate oxygen [step (6)]. This proton shift is probably intramolecular in view of the favourable geometric orientation of the α-alkyl hydrogen with respect to the sulphate group provided that the structure of the intermediate (III) tends to the *cis* ' boat ' structure established for 10-isopropyl-9-isopropylidene-9,10-dihydroanthracene.[2a]

The mechanism for the formation of the sultone (6l) from 1,4,9-trimethylanthracene is shown in Scheme 3. The initial step is the addition of SO_3 to C-1 leading to the intermediate (IV). The 1,2-hydride shift from the methyl-carbon at C-11 towards C-1 [step (8)] then yields (V) which dipolar intermediate on ring closure leads to the sultone (6l). The steps (8) and (9) resemble those proposed for the formation of the seven-membered sultones (8) (see above). The mechanism for the formation of (6m) is analogous but with the initial addition of SO_3 at C-4.



SCHEME 2

Reactive Sites and Relation to Protonation Studies.— The greatest variety in products is observed on reaction of the substituted 9-ethylanthracenes with dioxan–SO_3. 1-Chloro- (3e) and 1,5-dichloro-9-ethylanthracene (3f) yield the dimers (5e) and (5f) respectively, whereas 4-chloro-9-ethylanthracene (3g) yields, just like 9-ethylanthracene, the two sulphonic acids (4g) and (7g); finally 4,5-dichloro-9-ethylanthracene (3h) gives no reaction at all.



SCHEME 3

These differences in product formation can be explained in terms of the assumption that (3e) and (3f) only yield products resulting from the secondary 9-anthracenium-9-sulphonate (C-9 sulphonated σ-complex), whereas (3f) gives only products resulting from the more stable tertiary 10-anthracenium-10-sulphonate (C-10 sulphonated σ-complex). The origin for this difference in behaviour may be that (i) the side-chain sulphonated products [as obtained from (3g)] would give rise to a (too) large degree of steric strain between the 9-substituent and the 1-chlorine atom, (ii) there is a very substantial relief of steric strain between the ethyl group at C-9 and the 1-chlorine atom on addition of SO_3 at C-9 which is at least maintained (or may be even larger) in the products (5e) and (5f).* Such reasons for the formation of products resulting from the less stable 9-anthracenium-9-sulphonate are absent with (3g) as substrate and, in fact, only products resulting from the 9-anthracenium-10-sulphonate are observed.

The absence of product formation with 4,5-dichloro-9-ethylanthracene may be explained in terms of a too-low reactivity of this substrate towards dioxan–SO_3 as result of the two deactivating chloro-substituents in the substrate. In contrast 1,5- and 4,5-dichloro-9-methylanthracene do yield side-chain sulphonated products on reaction with dioxan–SO_3, indicating a higher reactivity of these two substrates.† Protonation of (3e) and (3f)

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* The geometry of the central ring in (5e) and (5f) is thought to resemble the *cis* ' boat ' structure established for 10-isopropyl-9-isopropylidene-9,10-dihydroanthracene.[2a]

† A higher reactivity of the methyl as compared with the ethyl group is also evident in the reaction of 9-ethyl-10-methylanthracene with dioxan–SO_3, the only product being 9-ethyl-10-anthrylmethanesulphonic acid.[9] Suzuki observed the same difference in reactivity of the two alkyl groups in the nitration of 9-ethyl-10-methylanthracene.[10]

with FSO_3H leads to the formation of both the C-9 and the C-10 protonated carbenium ions, whereas protonation of (3g) and (3h) yields only the latter ions.[7] These results are in agreement with those obtained for the sulphonation of these compounds.

The investigated 9-methylanthracenes (1)—(4) all yield side-chain α-sulphonic acids, resulting from initial attack of SO_3 at C-10 (see above) and all these substrates on reaction with FSO_3H yield exclusively the C-10 protonated ions. However, 1,5-dichloro-9-methylanthracene (3c) on reaction with dioxan–SO_3 yields also the dimer (5c) which eventually results from initial attack of SO_3 at C-9. The additional formation of (5c) must be due to a delicate balance of a variety of factors. The same applies to the formation of the sultones (6l and m) from 1,4,9-trimethylanthracene as these sultones result from initial attack of SO_3 at C-1 and C-4.

Protonation of 1-chloro-(3i) and 1,5-dichloro-9-isopropylanthracene (3j) yields both the C-9 and C-10 protonated carbenium ions. Accordingly these compounds on reaction with dioxan–SO_3 are expected to form products resulting from initial attack of SO_3 at C-9 as well as products resulting from attack of SO_3 at C-10 and, in fact they do, *viz.* (5i) and (5j) respectively on the one hand and all other obtained products on the other.

In contrast to the absence of products eventually resulting from initial attack of SO_3 at C-10 with 1-chloro- and 1,5-dichloro-9-ethylanthracene as substrate, these kinds of products do result with the 9-isopropyl homologues (3i) and (3j). This can be explained in terms of (i) the lower degree of relief of steric strain on C-9 sulphonation of (3i) and (3j) as compared with for example 1-chloro-9-ethylanthracene in view of the presence of the larger alkyl group at C-9 (isopropyl *vs.* ethyl) and (ii) the high stability of (9i) and (9j) (for a discussion on stable 9-alkylidene-9,10-dihydroanthracene derivatives see the introduction) which compounds are the intermediates in the formation of (10i)—(12i) and (10j)—(12j) respectively.

TABLE 2

^1H N.m.r. data of the dimeric products in [$^2H_8$]dioxan [a]

Chemical shifts δ (p.p.m.) and multiplicities (Hz)

Compound	Methine H	Vinylic H	Methyl H
(5c)	5.4 (m)	7.5—7.0	
(5e)	4.2 (m)	6.9—6.2	2.55—2.15 (doublets J = 7)
(5f)	4.95 (m)	6.9—6.3	2.55—2.15 (doublets J = 7)
(5i)	4.2 (m)		2.5—2.3 (singlets)
(5j)	5.1 (m)		2.5—2.3 (singlets)

[a] The aromatic protons exhibit multiplets in the range 7.9—6.3 p.p.m.

TABLE 3

^1H N.m.r. data of the seven-membered ring sultones (8i—k) and of the sulphonic acids (9i—j) in [$^2H_8$]dioxan [a]

Chemical shifts [b]

Compound	9-H [c]	10-H [c]	CH_3	
(8i)	4.76	5.81	1.53	1.60
(8j)	4.78	6.23	1.53	1.59
(8k) [d]	4.10	5.74	1.53	1.53
(9i)		5.85	2.07	2.18
(9j)		6.36	2.07	2.18

[a] The positions of the aromatic protons are unknown in view of the complexity of the absorption pattern. [b] All singlet absorptions. [c] 9-H and 10-H represents the protons attached to the central ring, at the side of the alkyl group and the SO_2 moiety or SO_3H group respectively. [d] F. van de Griendt and H. Cerfontain, *J.C.S. Perkin II*, 1980, 19.

TABLE 4

^1H N.m.r. data of the obtained unsaturated (pyro)-sulphonic acids and the 9-allylanthracenes (10i—k) in [$^2H_8$]dioxan [a]

Chemical shifts (δ) and multiplicities

Compound	10-H	H–C(α)	H–C(β)	H–C(α)′
(7g)			7.26 (d, J = 16, 1 H)	
[b]		8.61 (d, J = 16, 1 H)	7.26 (d, J = 16, 1 H)	
(10i)	8.73 (s)		5.26 (s, 1 H) 5.85 (s, 1 H)	2.59 (s, 3 H)
(10j)	9.04 (s)		5.26 (s, 1 H) 5.85 (s, 1 H)	2.56 (s, 3 H)
(10k) [c]	8.50 (s)		5.27 (s, 1 H) 5.89 (s, 1 H)	2.37 (s, 3 H)
(11i)	8.66 (s)			2.72 (s, 3 H)
(11j)	9.11 (s)			2.70 (s, 3 H)
(11k) [c]			6.86 (s, 1 H)	2.81 (s, 3 H)
(12i)	8.66 (s)			4.67 (s, 2 H)
(12j)	9.02 (s)			4.75 (s, 2 H)
(12k) [c]	8.60 (s)		5.78 (3, 1 H) 6.50 (s, 1 H)	4.59 (s, 2 H)

[a] The protons H(1,4,5,8) and H(2,3,6,7) exhibit absorptions in the range 9.0—8.0 and 7.8—7.3 p.p.m. respectively. [b] Data from (*E*)-1-(9-anthryl)ethenesulphonic acid.[3a] [c] See footnote *d* of Table 3.

EXPERIMENTAL

Materials.—All compounds were prepared from reaction of the appropriate Grignard reagents and anthrones as described before.[3] 1,4-Dimethylanthrone was obtained from commercially available 1,4-dimethylanthraquinone according to a literature procedure.[11] The ^1H n.m.r. data of the substrates were reported before.[7]

Reaction Procedure.—The reactions of the substrates with dioxan–SO_3 complex were carried out as described previously at a temperature of 25 °C.

Spectrometers.—The 100 MHz ^1H n.m.r. spectra were recorded with a Varian HA-100 spectrometer equipped with a variable-temperature probe, and the 60 MHz ^1H n.m.r. spectra with a Varian A60 spectrometer. The chemical shifts of the products are relative to external neat tetramethylsilane (capillary), those of the substrates relative to internal tetramethylsilane.

The ^{13}C n.m.r. spectra were obtained using a Varian XL-100 spectrometer, in 12-mm tubes at 25.2 MHz, with and without proton-noise decoupling. Chemical shifts are relative to internal $CDCl_3$ and converted to the $SiMe_4$ scale.

The 70 eV EI mass spectra were recorded on a AEI MS 902 with a direct insertion probe. The FI and FD mass spectra were recorded on a Varian MAT 711 double focusing mass spectrometer equipped with a combined EI/FI/FD source. For the FD experiments emission-controlled FD was used at a threshold of 4 nA and the samples were loaded with the dipping technique ($CDCl_3$-solution). The FI measurements were obtained with a direct insertion probe. The i.r. spectra ($CHCl_3$ and KBr) were recorded on a Perkin-Elmer 177 spectrometer.

[9/740 *Received*, 14*th May*, 1979]

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