

Aromatic Sulphonation. Part 79.¹ Sulphonation of Some (Poly)-methylantracenes with Dioxan-Sulphur Trioxide Complex in Dioxan

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The reactions of 2-MeA (2-methylantracene), 2,3-Me₂A, 2,3,6,7-Me₄A, 1-MeA, 1,2-Me₂A, 1,3-Me₂A, and 1,4-Me₂A with 1.5 equiv. dioxan-SO₃ complex in dioxan at 40 °C lead in general to the formation of monosulphonic acids. The first three substrates yield the *meso*-sulphonic acids and 1-MeA and 1,2-Me₂A products with the sulphonic acid group at the 4- and 10-position. The reaction of 1,3-Me₂A at 17 °C leads to an equilibrium mixture of unconverted substrate and the 1,3-dimethylantracene-4-, -9-, and -10-sulphonate σ -complexes. On warming this reaction mixture to 40 °C, 1,3-dimethylantracene-4- and -10-sulphonic acid and the sultone (1) are formed. 1,4-Me₂A at 17 °C yields a mixture of unconverted substrate, and 1,4-dimethylantracene-9- and possibly -1-sulphonate σ -complexes. Warming this mixture to 40 °C leads to the formation of 1,4-dimethylantracene-2-, -5-, and -6-sulphonic acid. The positional order for sulphonation is in agreement with that predicted by the localization energies, provided that allowance is made for steric factors.

PROTIC sulphonation of anthracene with several sulphonating reagents has received considerable attention.² Recently Morley reinvestigated the sulphonation with chlorosulphuric acid both in neutral and basic solvents,³ and in acetic acid and related solvents.⁴ Some of his results differed from those reported previously. Morley established that the reaction of anthracene with chlorosulphuric acid in neutral or basic solvents yields a mixture of anthracene-1-, -2-, and -9-sulphonic acids, anthracenedisulphonic acids, 9-chloroanthracene, 9,9'-bianthryl, and anthracene polymers. The formation and the yield of each product depends on the experimental conditions and the solvent used. In the basic solvent systems reversible sulphonation at the 9-position is accompanied by irreversible sulphonation at the 1- and 2-positions. Sulphonation of anthracene with either chlorosulphuric acid and acetic acid or sulphuric acid and acetyl chloride yields a mixture of anthracene-1- and -2-sulphonic acid, anthracenedisulphonic acids, 9-chloroanthracene, and its monosulphonic acids. The reaction of anthracene with sulphuric acid and acetic anhydride gives the 1-, 2-, and 9-sulphonic acids together with some disulphonic acids.

9,10-Disubstituted anthracene derivatives, *e.g.* 9,10-dichloro-⁵ and 9,10-diphenyl-anthracene⁶ yield exclusively the 2-sulphonic acid as result of steric hindrance towards substitution at position 1.

Aprotic sulphonation of anthracene with dioxan-SO₃ complex leads to anthracene-9-sulphonic acid together with small amounts of the 1- and 2-isomer.⁷ The 'sulphonation' of 9-alkylantracenes with the same sulphonating reagent yields in most cases side-chain sulphonated products.⁸ Only 9-*t*-butyl-⁹ and 9-neopentyl-anthracene^{8b} lead to other kinds of products, *i.e.* the former yields 10-*t*-butyl-9,10-dihydroanthracene 9,10-sultone and the latter a mixture of 9-neopentyl-anthracene-10- and -4-sulphonic acid (sulphonation of 9-phenylantracene also leads to formation of a mixture of mainly the 10- with some 4-sulphonic acid^{8a}).

In view of the absence of information on the aprotic sulphonation of (poly)methylantracenes, not substituted at the 9- or 10-position, we have studied the behaviour of some of these substrates on reaction with

dioxan-SO₃. This investigation is an extension of our studies on the sulphonation of methyl-substituted condensed polyaromatics (the sulphonation of 1-methyl-,¹⁰ 2-methyl-, and the dimethyl-naphthalenes¹¹ was recently reported).

In order to obtain information on the reactive site(s) for the formation of the initial intermediate (σ -complex) in electrophilic aromatic substitution we have also examined the protonation of (poly)methylantracenes.¹²

RESULTS

Reactions with Dioxan-SO₃ Complex in Dioxan.—Seven (poly)methylantracenes, *viz.* 1-MeA (methyl-anthracene), 2-MeA, 1,2-Me₂A, 1,3-Me₂A, 1,4-Me₂A, 2,3-Me₂A, and 2,3,6,7-Me₄A have been treated with [²H₈]dioxan-SO₃ complex in [²H₈]dioxan at 17 and 40 °C. The sulphonic acids obtained have been assigned on the basis of their ¹H n.m.r. data, which are listed in Table 1. The compositions of reaction mixtures were determined by ¹H n.m.r. multicomponent analysis.¹³

In all reactions (very) small amounts of unknown (probably polymeric) products have been formed. Most likely these products are oligoanthrylenes as these products were in fact obtained on sulphonation of anthracene under mild conditions.¹⁴

1-Methylantracenes.—At 17 °C 1-MeA is slowly converted into its sulphonic acids as the reaction mixture after *ca.* 20 min contained only 5 ± 2% 1-methylantracene-4-sulphonic acid. On warming the mixture to 40 °C the reaction mixture consisted of 90 ± 2% 1-methylantracene-4- and 10 ± 2% -10-sulphonic acid after *ca.* 25 min.

1,2-Me₂A reacted fast with dioxan-SO₃ as no unconverted substrate was found to be present after a reaction time of 40 min at 17 °C; the reaction mixture then consisted of 85 ± 2% 1,2-dimethylantracene-4- and 15 ± 2% -10-sulphonic acid. No changes in composition have been observed on warming the mixture to 40 °C.

The ¹H n.m.r. spectrum of the reaction mixture of 1,3-Me₂A at 17 °C showed remarkable observations, *viz.* (i) very broad absorptions for H(4), H(9), and H(10) (half-width *ca.* 50 Hz), (ii) broad absorptions for the α - and β -methyl protons (half-width *ca.* 30 and 15 Hz, respectively), (iii) relatively sharp signals for the remaining aromatic protons, and (iv) some small sharp signals assigned to absorptions of 1,3-dimethylantracene-10- and -4-sulphonic acid. The first three spectral features can be accounted for by assuming

TABLE 1

¹H N.m.r. data of the (poly)methylanthracenesulphonic acids in [2H₆]dioxan ^a

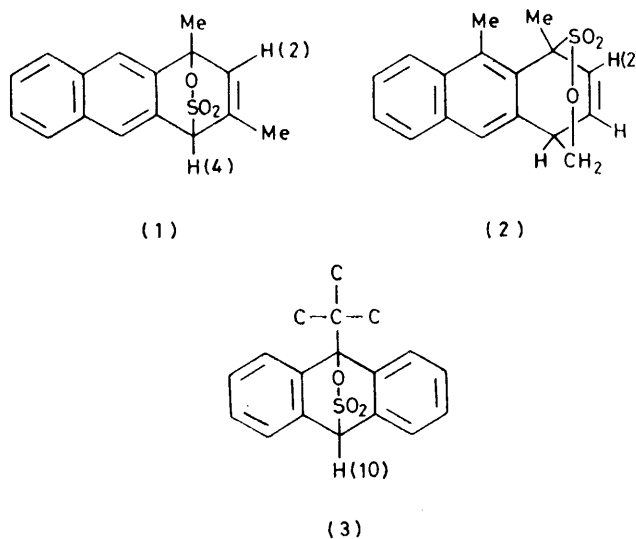
Methyl	Anthracene substituents Sulphonic acid	CH ₃ ^{b,c}	H(1) ^c	H(2)	H(3)	H(4)	Ring position (δ)		H(7)	H(8)	H(9) ^c	H(10) ^c
							H(5)	H(6)				
1	4	3.03		7.54(d)	8.38(d)		8.31(m)	7.75(m)	7.75(m)	8.31(m)	8.76	9.46
	10	2.99				9.33(d)	9.46(d)			8.48(d)	9.09	
1,2-Di	4	2.85(1) 2.66(2)			8.25(s)		8.25(m)	7.69(m)	7.69(m)	8.25(m)	8.78	9.35
	10	2.83(1) 2.63(2)				9.18(d)	9.40(d)				9.02	
1,3-Di	4	2.91(1) 3.03(3)		7.28(s)			ca. 8.2(m)			ca. 8.2(m)	8.64	9.63
	10	2.91(1) 2.70(3)		7.36(s)		9.08(s)	9.42(d)	7.70(m)	7.70(m)	8.21(d)	8.95	
1,4-Di	2	3.29(1) ca. 2.88(4)			7.98(s)		8.40(d)	7.68(m) ^d	7.68(m) ^d	8.49(d)	8.70	8.61
	5	ca. 2.88(1,4)		7.47(s)	7.47(s)			8.18(m) ^d	7.68(m) ^d	8.18(m) ^d	8.87	9.51
2	6	ca. 2.88(1,4)		7.45(s)	7.45(s)				7.93(d)			
	9	2.75	9.21		7.71(m) ^d	8.09(d)	8.18(d)	7.71(m) ^d	7.71(m) ^d	9.43(d)		8.81
2,3-Di	10	2.66				9.34(d)	9.34(d)				8.73	
	9	2.66(2) 2.56(3)	9.16			7.82(s)	8.12(d)	7.67(m)	7.67(m)	9.40(d)		8.63
2,3,6,7-Tetra	9	2.54(2,6) 2.44(3,7)	9.13			7.80(s)	7.80(s)			9.13(s)		8.47

^a Only positively assigned absorptions are listed. ^b The numbers in parentheses represent the position of the methyl group. ^c All singlet absorptions. ^d Centre of unresolved multiplet.

equilibria between 1,3-Me₂A and the 1,3-dimethylanthracenium-4-, -9-, and -10-sulphonate σ -complexes, which are rapid on the ¹H n.m.r. time scale. At 17 °C the reaction mixture of 1,3-Me₂A after ca. 30 (50) min was found to contain 85 ± 3 (63 ± 3)% of an equilibrium mixture of 1,3-Me₂A and the three σ -complexes, 11 ± 3 (28 ± 3)% 1,3-dimethylanthracene-10-, and 4 ± 3 (9 ± 3)% -4-sulphonic acid. On warming the mixture to 40 °C it consisted, after ca. 20 min, only of sulphonic acids and a sultone, viz. 73 ± 3% 1,3-dimethylanthracene-10-, 14 ± 3% -4-sulphonic acid, and 13 ± 3% of the sultone (1). With longer reaction times no changes in composition have been observed. The structure of the sultone (1) has been assigned tentatively on the basis of two singlet absorptions at δ 6.89 and 6.02 due to H(2) and H(4), respectively. The chemical shifts of the absorptions of H(2) and H(4) are in good agreement with those observed at δ 6.85 for H(2) in sultone (2) ¹ and at 5.99 for H(10) in sultone (3),⁹ respectively. The methyl absorptions of (1) appear as singlet absorptions at δ 2.65 and 2.76. In the ¹H n.m.r. spectrum of 1,4-Me₂A at 17 °C again very broad signals are observed for the *meso*- and the methyl protons. This can be explained in terms of equilibria between 1,4-Me₂A and the 1,4-dimethylanthracenium-9- and possibly -1-sulphonate σ -complex(es). After warming to 40 °C the reaction mixture consisted, after ca. 20 min, of 49 ± 4% 1,4-dimethylanthracene-2-, 38 ± 4% -5-, and 13 ± 3% -6-sulphonic acid. For longer reaction times no change in this composition was observed.

2-Methylanthracenes.—On reaction of 2-methylanthra-

cenes, viz. 2-MeA, 2,3-Me₂A, and 2,3,6,7-Me₄A, with dioxan-SO₃ complex at 17 °C, after ca. 30 min heterogeneous solutions were obtained containing mainly the unconverted



substrate. On warming the reaction mixtures to 40 °C clear solutions were obtained. For 2-MeA a clear solution was obtained after ca. 60 min; it consisted of 75 ± 3% 2-methylanthracene-9- and 18 ± 3% -10-sulphonic acid, and

TABLE 2

Localization energies of anthracene and its (poly)methylanthracenes

Anthracene substituents	Ring position									
	1	2	3	4	5	6	8	9	10	
^a	2.25	2.40								
1-Me				2.1295	2.2187		2.2312	2.013	2.0158	1.9831
1,2-Me ₂				2.1186	2.2166		2.2158	1.9762	1.9784	
1,3-Me ₂		2.2509		2.0305	2.2068		2.2318	2.0175	1.9537	
1,4-Me ₂	2.1295	2.2620			2.2164	2.4024		1.9740		
2-Me	2.1201		2.3952	2.2320	2.2307		2.2187	1.9823	2.0138	
2,3-Me ₂	2.1308				2.2199			1.9861		
2,3,6,7-Me ₄	2.1217							1.9594		

^a Data from A. Streitwieser, jun., 'Molecular Orbital Theory for Organic Chemists,' Wiley, New York, 1961, ch. 11.

$7 \pm 2\%$ unconverted substrate. For longer reaction times no change in composition was observed. 2,3-Me₂A and 2,3,6,7-Me₄A yielded clear solutions after reaction times of *ca.* 45 and 60 min, respectively. Both reaction mixtures contained exclusively the 9-sulphonic acid.

The localization energies for various reactive positions of the substrates investigated here have been calculated by the simple Hückel π -electron molecular orbital treatment as described previously.¹² The values obtained are reported in Table 2.

DISCUSSION

From the study on the aprotic sulphonation of the dimethylnaphthalenes it was concluded that the positional order for this type of electrophilic aromatic substitution is in good agreement with that predicted by the localization energies, calculated by the simple Hückel molecular orbital treatment, provided that allowance is made for steric factors.^{11b} An important factor in the aprotic sulphonation of these substrates is the steric hindrance towards α -substitution, which is present even in naphthalene itself, as can be seen from the observation of a primary kinetic isotope effect for this substrate of k_H/k_D , 1.9.¹⁵ This effect is assigned to the steric repulsion between the *peri*-hydrogen and the sulphonyl group on formation of the sulphonate from the preceding σ -complex. The reduction in α -substitution as a result of steric hindrance becomes more pronounced if an adjacent β -methyl group is present and such substitution does not occur at all in the presence of a *peri*-methyl group.

With anthracene the localization energies predict the following reactivity order: *meso* > α > β .¹⁶ This is in agreement with the observed substitution distribution for anthracene in reaction with dioxan-SO₃, being 66% 9-, 26% 1-, and 8% 2-substitution. As this ratio does not alter at prolonged reaction times and since it is independent of the substrate conversion this isomer ratio is kinetically controlled.^{8a} The predicted reactivity order in anthracene is further apparent from (i) the observed partial rate factors for protioderitiation (1.27×10^7 , 7 900, and 1 135 for the 9-, 1-, and 2-position respectively),¹⁷ (ii) protonation occurs exclusively at the *meso*-position,¹⁸ and (iii) benzylation which yields 9-benzoylanthracene as the main reaction product.¹⁹

In the anthracene system steric hindrance is to be expected both for *meso*- and α -substitution. The sulphonyl group in anthracene-9-sulphonic acid is very labile because of steric interaction with the two adjacent hydrogen atoms at the 1- and 8-positions. The formation of the 9-isomer was in fact found to proceed with a maximal substrate kinetic isotope effect (k_H/k_D , *ca.* 7) in the aprotic sulphonation with dioxan-SO₃ complex.^{7a} In view of the structural similarity of the α -positions of naphthalene and anthracene,* corresponding steric hindrance towards α -substitution in the anthracene

system is to be expected as in the naphthalene system (see above). This has in fact been observed as (i) the sulphonation of 9,10-dichloro- and 9,10-diphenylanthracene yield exclusively the 2-sulphonyl acids,^{5,6} (ii) the *t*-butylation of 9,10-dimethylantracene yields 9,10-dimethyl-2,6-di-*t*-butylantracene,²² and (iii) the acetylation of 9-methylantracene yields a mixture of 2-, 3-, 4-, and 10-acetyl-9-methylantracene.²³

The presently investigated 2-methylantracenes, *viz.* 2-MeA, 2,3-Me₂A, and 2,3,6,7-Me₄A, all yield exclusively the *meso*-sulphonyl acid(s), and no α -substitution has been observed. On the basis of the localization energies the reactivity order for the positions of 2-MeA would be $9 > 10 > 1$ (see Table 2). In fact, 2-MeA yields 75% 2-methylantracene-9- and 18% -10-sulphonyl acid. For a discussion on the absence of the 1-sulphonyl acids from 2-MeA, 2,3-Me₂A, and 2,3,6,7-Me₄A, see later.

The products obtained in the sulphonation of these three substrates are in good agreement with those predicted on the basis of the protonation of the substrates. 2-MeA yields 93% of the 2-methyl-9- and 7% of the -10-anthracenium ion, and 2,3-Me₂A and 2,3,6,7-Me₄A yield exclusively the 9-anthracenium ions.

1-MeA (1,2-Me₂A) yields 80 (85)% 4- and 20 (15)% 10-sulphonyl acid. From the localization energies the reactivity order predicted for 1-MeA is $10 > 9 > 4$ and for 1,2-Me₂A $9 \geq 10 > 4$ (see Table 2). The absence of the 9-sulphonyl acids can be explained in terms of the prevention of α -substitution by the *peri*-methyl group in the 1-position. This corresponds to the complete absence of α -substitution in the dimethylnaphthalenes.¹¹ In view of the small difference in $\Delta L^+_{10,4}$ for 1-MeA and 1,2-Me₂A (0.1464 and 0.1402, respectively) only small variations in the isomer distribution for these two compounds are to be expected. This is in fact observed. However, from the differences in localization energies for the 10- and 4-positions a reversed ratio for sulphonyl acid formation would be expected. The observed ratio indicates that the steric factor is greater for the 10- than the 4-position.

The reaction of 1,3-Me₂A yields initially an equilibrium mixture of unconverted substrate and three 'anthracenium ions' resulting from attack of SO₃ at the 4-, 9-, and 10-positions [*i.e.* the sites at which attack is to be expected on the basis of the localization energies (see Table 2)]. On warming the reaction mixture to 40 °C 73% 1,3-dimethylantracene-10-, 14% -4-sulphonyl acid, and 13% sultone (1) are obtained. These observations demonstrate the course of the electrophilic aromatic substitution reaction; the first step is the transfer of SO₃ from the dioxan-SO₃ complex to the most reactive sites of the substrate, leading to the various σ -complexes, and in the following step(s) the products are formed. As to product formation various reaction paths apply depending on steric and electronic factors in the anthracene system. The initially formed 1,3-dimethylantracene-4-sulphonyl acid leads to the formation of two products, *viz.* 1,3-dimethylantracene-4-sulphonyl

* For example the C(1)-C(2) distances are 1.361 Å for naphthalene²⁰ and 1.375 Å for anthracene,²¹ and the C(1)-C(8) distances (calculated from the reported X-ray studies^{20,21}) are both *ca.* 2.50 Å.

acid, resulting from the abstraction of H(4) as a proton, and sultone (1), resulting from ring closure between the oxygen of the sulphate group and the carbon at position 1. 1,3-Dimethylantracene-10-sulphonate leads to the formation of 1,3-dimethylantracene-10-sulphonic acid (proton abstraction) and 1,3-dimethylantracene-9-sulphonate leads to the formation of 1,3-dimethylantracene (loss of SO_3) in view of the steric interaction which would result upon abstraction of H(9) between the sulfo-group at C(9) and the methyl group at C(1).

The presence of substitution at an α -position having an adjacent β -methyl group is due to a delicate balance between the electronic factors which favour this substitution (as indicated by the relative localization energies) and the steric hindrance of the adjacent β -methyl group. This may be concluded from the following observations: (i) 1,3-Me₂A yields *e.g.* 1,3-dimethylantracene-4-sulphonic acid ($L_4^+ 2.0305$), (ii) the absence of 1-sulphonic acids in the reactions of 2-MeA, 2,3-Me₂A, and 2,3,6,7-Me₄A (for 2-MeA $L_1^+ 2.1201$), and (iii) the formation of 1-methylantracene-4-sulphonic acid from 1-MeA which has about the same value for the localization energy at the 4-position ($L_4^+ 2.1295$) as at the 1-position of 2-MeA.

The features of the ¹H n.m.r. spectra of the reaction mixture obtained by treatment of 1,4-Me₂A with dioxan-SO₃ complex at 17 °C (broad signals for the *meso*- and the methyl protons) can be explained by equilibria between 1,4-Me₂A and 1,4-dimethylantracene-9- and/or -1-sulphonate σ -complexes. In fact, these are the positions predicted by localization energies for initial attack of the electrophile.

In view of the localization energies for the 2-, 5-, and 6-positions of 1,4-Me₂A (2.2620, 2.2164, and 2.4024, respectively) the amount of 1,4-dimethylantracene-2-sulphonic acid formed (48%) seems rather high. This also applied to the quantity of 1,4-dimethylnaphthalene-2-sulphonic acid obtained from 1,4-dimethylnaphthalene.¹¹ For reasons of the high reactivity of the 1-position of this substrate and the possibility of a 1,2-sulpho-shift it was suggested that the formation of 1,4-dimethylnaphthalene-2-sulphonic acid results (in part) from the *ipso*- σ -complex.¹¹ A comparable great difference in reactivity is observed between the *ipso*- and the 2-position of 1,4-Me₂A ($\Delta L_{1,2}^+ 0.1325$ versus 0.1269 for 1,4-dimethylnaphthalene¹¹). Additional evidence in favour of this *ipso*-attack was found in the formation of sultone (2) from 1,4,9-Me₃A.¹ It has been proposed that this sultone results from initial *ipso*-attack of SO₃ at C(1). Apparently the 'escape routes' from the *ipso*- σ -complexes for 1,4-Me₂A and 1,4,9-Me₃A are different; the former σ -complex leads to the 2-sulphonic acid whereas the latter yields the sultone (2) (possibly to avoid a *peri*-methyl-methyl interaction).

1,4-Dimethylantracene-5- and -6-sulphonic acid are believed to result from direct attack of SO₃ at these positions, as has been observed for the sulphonation of anthracene with dioxan-SO₃. Accordingly, about the

same α : β isomer ratio is to be expected as for anthracene;⁷ this is in fact observed (3.3 versus 2.9).

Protonation of the substituted 1-methylantracenes only yields the C(9)- and/or C(10)-protonated anthracenium ions, indicating that these positions are the most reactive ones. In the sulphonation reactions of these substrates other positions (for example the 4-position) are favoured. This again illustrates the great steric hindrance towards *meso*-substitution (see above).

EXPERIMENTAL

Materials.—The substrates (and their ¹H n.m.r. data) were obtained as described before.¹²

Reaction Procedure.—The reactions of the substrates with 1.5 equiv. dioxan-SO₃ complex were carried out as described previously^{8b} at temperatures of 17 and 40 °C.

Spectrometer.—The 100 MHz ¹H n.m.r. spectra were recorded with a Varian HA-100 spectrometer equipped with a variable temperature probe. The chemical shifts of the products are relative to external neat tetramethylsilane (capillary).

We thank Dr. V. Štěpán, Institute of Macromolecular Chemistry of the Czechoslovakian Academy of Sciences, Prague, for gifts of 1,3-di-, 2,3-di-, and 2,3,6,7-tetra-methylantracene.

[9/995 Received, 25th June, 1979]

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