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AROMATIC PROTONATION.—3[1]

^{1}H NMR PARAMETERS OF SOME METHYL SUBSTITUTED ANTHRACENIUM IONS. STUDY ON THE SITE OF PROTONATION

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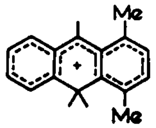
Abstract—1-Methylanthracene (1-MeA), 2-MeA, 1,2-Me_2A, 1,3-Me_2A, 1,4-Me_2A, 2,3-Me_2A, 1,4,9-Me_3A and 2,3,6,7-Me_4A have been protonated with FSO_3H in SO_2ClF as cosolvent at −78°. With all substrates C(10)- and/or C(9)-protonation was observed. The site of protonation of the hydrocarbons was found to depend on (i) the degree of mesomeric stabilisation of the positive charge of the resulting anthracenium ions by the Me substituents, and (ii) the relief of steric strain between H(9) and the *peri*-Me substituent at position 1 on protonation at C(9).

In relation to our studies on the sulphonation of the (poly)methylanthracenes with dioxan-SO_3,[2] we have protonated these hydrocarbons with the aim to obtain information on the reactive site(s) for the addition of the electrophile with formation of the σ-complex, as arenium ions are well established as intermediates in aromatic substitution. For example, some of the products resulting on sulphonation of α-chloro-9-alkylanthracenes were explained by initial attack of SO_3 at the position predicted on the basis of a protonation study of these compounds.[3]

With the exception of reports on the parent anthracenium ion[4] there is no literature information on the protonation of alkylanthracenes other than those substituted in the 9- and/or 10-position.

RESULTS

Eight Me-substituted anthracenes have been protonated with FSO_3H in SO_2ClF as cosolvent at −78°. ^{1}H NMR spectra of the obtained mixtures were recorded at −40°. The ^{1}H NMR parameters (Table 1) indicated that (i) 1,4-dimethylanthracene (1,4-Me_2A), 2,3-Me_2A, 1,4,9-Me_3A and 2,3,6,7-Me_4A yield exclusively the C(10)-protonated ions **1**, **2**, **3** and **4** respectively (see Compound sheet), (ii) 1,2-Me_2A yields exclusively the C(9)-protonated ion **5**, and (iii) 1-MeA, 2-MeA and 1,3-Me_2A yield a mixture of the C(10)-protonated ions (25% **6**, 7% **8** and 94% **10** respectively) and the C(9)-protonated ions (75% **7**, 93% **9** and 6% **11** respectively).



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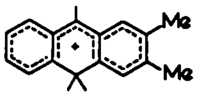

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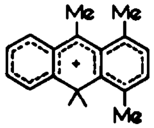

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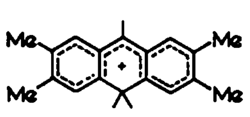

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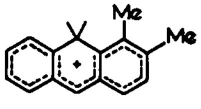

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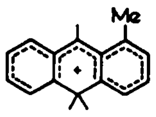

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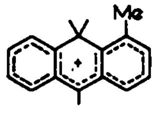

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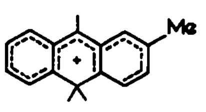

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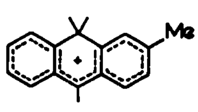

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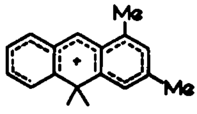

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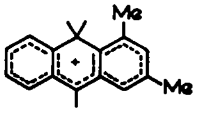

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Table 1. ^{1}H NMR data of the 9- and 10-anthracenium ions

Carbenium ion	Chemical shifts (p.p.m.) and multiplicities (Hz).										
no.	CH$_3$[a,b]	CH$_2$[a]	H(9)or H(10)[a]	H(1)[a]	H(2)	H(3)	H(4)	H(5)	H(6)	H(7)	H(8)
1	3.10(1) 2.70(4)	4.90	10.22		7.79(d) J=8	[c]		8.39(d) J=8	[c]	[c]	8.60(d J=8
2	2.64(2) 2.81(3)	5.04	9.70	8.29			8.05(s)	[c]	[c]	7.98(t) J=8	8.48(d J=8
3	3.08(1) 2.70(4) 3.86(9)	4.79			7.82(d) J=8	[c]		[c]	[c]	[c]	8.80(d J=8
4	2.65(2,7) 2.79(3,6)	4.94	9.52	8.23			8.01(s)	8.01(s)			8.23(s
5	2.70(1) 2.90(2)	4.95	9.76			7.94(d) J=8	8.40(d) J=8	[c]	[c]	8.01(t) J=8	8.52(d J=8
6	3.10(1)	5.15	10.24		7.85(d) J=8	[c]	[c]	[c]	[c]	[c]	[c]
7	2.80(1)	4.91	9.97		[c]	[c]	8.52(d) J=8	8.61(d) J=8	[c]	[c]	[c]
8	2.73(2)	5.10	9.90	[c]		[c]	[c]	[c]	[c]	[c]	[c]
9	2.88(2)	5.08	9.79	8.08		7.91(d) J=8	8.48(d) J=8	8.52(d) J=8	8.00(t) J=8	8.21(t) J=8	8.35(d J=8
10	3.08(1) 2.86(3)	5.07	10.06		7.76(s)		7.93(s)	8.33(d) J=8	[c]	[c]	8.54(d J=8
11	2.80(1) 2.76(3)	4.97	9.92		[c]		[c]	[c]	[c]	[c]	[c]

[a] All Singlet absorptions.

[b] The numbers between brackets indicate the positions of the methyl groups.

[c] Unresolved absorptions between 8.7 and 7.7 ppm.

The assignment of the C(9)- and/or C(10)-protonated ions (with exception of **3**) is based on the presence of a low field singlet absorption between 10.2 and 9.5 ppm for H(10) or H(9) respectively. The assignment of **3** is based on the chemical shift of the Me absorption at 3.86 [assigned to Me-C(9)], which value is in good agreement with that of 3.98 reported for the 1-chloro-9-methyl-10-anthracenium ion.[1]

The assignment of the other aromatic protons of the various ions is based on their multiplicities. Assignments of absorptions with the same multiplicity have been made on the basis of the anticipated deshielding of the protons bonded to carbons (or protons of a Me group) which are formally conjugated with the positive charge of the ion relative to those which are bonded to carbons which occupy positions which are not conjugated with the positive charge.

The ions **6** and **7**, both obtained from 1-MeA, have been assigned on the basis of the chemical shift differences between their low field singlet absorptions (at 10.24 and 9.97 respectively) and the Me absorptions (at 3.10 and 2.80 respectively). The H(9) absorption of **6** (and also that of **1**) is shifted 27 (25) Hz downfield relative to the H(10) absorption of **7** as result of a *peri*-Me interaction. The Me group in **6** occupies a position which carries a fractional positive charge as result of conjugation, whereas in **7** it is bonded to a position which is not conjugated with the positive charge. This explains the chemical shift difference of 30 Hz observed between the methyl absorptions of these two ions.

The assignment of the ions **10** and **11** is based on similar arguments: the absorption of H(9) in **10** is shifted 14 Hz down field relative to that of H(10) in **11** and a chemical shift difference is observed between both the α- and β-Me protons of **10** and **11**, *viz* of 28 and 10 Hz respectively.

2-MeA yields the ions **8** and **9**. Their assignment is based on the chemical shift difference of their Me absorptions (which are at 2.88 and 2.73 ppm respectively). The Me group in ion **8** occupies a position which carries a fractional positive charge as result of conjugation, whereas in **9** it is bonded to a position which is not conjugated with the positive charge. Accordingly the Me absorption at 2.88 is assigned to the ion **9**.

The localisation energies for the 9- and 10-positions of 1- and 2-MeA have been calculated with the simple Hückel π-electron MO treatment, utilising the inductive model for the Me substituent with $\delta\alpha_r = -0.3$, where r represents the position which is occupied by the Me substituent.[5,6] They were found to be for 1-MeA $L_9^+ = 2.016\beta$ and $L_{10}^+ = 1.983\beta$ and for 2-MeA $L_9^+ = 1.982\beta$ and $L_{10}^+ = 2.014\beta$.

DISCUSSION

For electrophilic reactions the 9-position of anthracene is far more reactive than the 1- and 2-positions. For example (i) the differences in localisation energies for addition of the electrophile at the 9-position of anthracene on the one hand, and of the 1 and 2 position on the other, are high ($\Delta L_{9,1}^+ = 0.24\beta$ and $\Delta L_{9,2}^+ = 0.39\beta$ respectively[7]), (ii)

Table 2. ^{1}H NMR data of the substrates in $CDCl_3$

Substrate	Chemical shifts (p.p.m.) and multiplicities (Hz)										
	CH_3^{a,b}	H(1)	H(2)	H(3)	H(4)	H(5)	H(6)	H(7)	H(8)	H(9)^{b}	H(10)^{b}
1-MeA.	2.71(1)		7.30(m)^{c}	7.30(m)^{c}	7.90(m)^{c}	7.90(m)^{c}	7.30(m)^{c}	7.30(m)^{c}	7.90(m)^{c}	8.45	8.32
2-MeA.	2.42(2)	7.63(s)		7.17(d) J=9.0	7.83(m)^{c}	7.83(m)^{c}	7.31(m)	7.31(m)^{c}	7.83(m)	8.25	8.19
1,2-Me_2A.	2.63(1) 2.44(2)			7.17(d) J=8.5	7.70(d) J=8.5	7.91(m)	7.34(m)	7.34(m)	7.91(m)	8.46	8.26
1,3-Me_2A.	2.67(1) 2.40(3)		7.04(s)		7.48(s)	7.88(m)	7.35(m)	7.35(m)	7.88(m)	8.36	8.16
1,4-Me_2A.	2.71(1,4)		7.13(s)	7.13(s)		7.97(m)	7.42(m)	7.42(m)	7.97(m)	8.46	8.46
2,3-Me_2A.	2.46(2,3)	7.74(s)			7.74(s)	7.95(m)	7.40(m)	7.40(m)	7.95(m)	8.28	8.28
1,4,9-Me_3A.	2.90(1) 2.70(4) 3.18(9)		7.09(s)	7.09(s)		7.94(m)	7.44(m)	7.44(m)	8.21(m)		8.35
2,3,6,7-Me_4A	2.35(2,3,6,7)	7.60(s)			7.60(s)	7.60(s)			7.60(s)	8.04	8.04

[a,b]See the corresponding subscripts of Table 1.

[c]Center of unresolved multiplet.

the protonation occurs exclusively at C(9)[4], and (iii) the partial rate factors for protiodetritiation for the 1-, 2- and 9-positions are 7900, 1135, and 1.27×10^{7} respectively.[8] Accordingly it is to be expected that the investigated substrates are protonated exclusively at C(9) and/or C(10), and this is in fact observed.

With the dimethylnaphthalenes the site of protonation could very well be predicted on the basis of the localisation energies.[5] In order to discriminate between protonation of the methylanthracenes at C(9) or C(10) we have therefore calculated the localization energies for the 9- and 10-positions of 1- and 2-MeA.

The difference in localisation energies of the 9- and 10-position of 2-MeA ($\Delta L^{+}_{9,10} = 0.032\beta$) indicates preference for C(9)-protonation, as is in fact observed (93%). For 1-MeA $\Delta L^{+}_{10,9} = 0.033\beta$ and accordingly C(10)-protonation is to be expected. In fact the preferred site of protonation is however at C(9) as protonation of 1-MeA leads to a mixture of 75% **7** and 25% of **6**. The preference for the formation of ion **7** over **6** is ascribed to a dominating steric effect, *viz* relief of steric strain between H(9) and the Me substituent at C(1) on forming ion **7**.

Protonation of 1,2-Me_2A leads *exclusively* to the C(9)-protonated ion **5**. This can now be explained in terms of (i) relief of steric strain between H(9) and the Me substituent at C(1) on forming **5** (see just before) and (ii) the larger stabilisation of the ion **5** as compared with **7** as a result of the presence of the additional Me substituent at C(2) with the former ion.

Protonation of 1,3-Me_2A yields the ions **10** [with protonation at C(10)] and **11** [with protonation at C(9)] for 94 and 6% respectively, whereas 1-MeA yields the ions **6** [with protonation at C(10)] and **7** [with protonation at C(9)] for 7 and 93% respectively. This reversed ratio with 1,3-Me_2A is ascribed to the additional mesomeric stabilisation of the positive charge in **10** by the Me substituent at C(3).

Protonation of 1,4,9-Me_3A yields exclusively the "tertiary"† C(10)-protonated ion **3**. Apparently the relief of steric strain which would result on C(9)-protonation (loss of a *peri*-Me-Me interaction) is not sufficiently large to obtain the less stable "secondary" [C(9)-protonated] ion. This is in agreement with the observation of exclusive protonation at C(10) in 1-chloro- and 1,5-dichloro-9-methylanthracene.[1]

EXPERIMENTAL

Materials. 2-Methylanthracene, fluorosulphuric acid and sulphurylchloride fluoride were obtained commercially. 1-, 1,2-di- and 1,4-di-methylanthracene were prepared from their corresponding anthraquinones.[10] 1,4-Dimethylanthraquinone was obtained from Frinton; the other anthraquinones were prepared as described.[11] The preparation of 1,4,9-trimethylanthracene was reported.[3]

The ^{1}H NMR data of the substrates in $CDCl_3$ are given in Table 2.

Preparation of the anthracenium ions. Solns of the anthracenium ions were prepared by addition of *ca* 1 ml FSO_3H cooled to *ca* −78° to a cooled slurry of 100 mg of the hydrocarbon in *ca* 1 ml SO_2ClF at −78°. The resulting mixture was stirred vigorously until a clear soln was obtained.

^{1}H NMR *analysis.* The 100 MHz spectra were recorded with a Varian HA-100 spectrometer, equipped with a variable temp probe, at −40°. The chemical shifts (δ_H) are for the protonation mixtures relative to external neat TMS (capillary) and for the substrates relative to internal tetramethylsilane.

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† The description "tertiary" and "secondary" is used as the major part of the positive charge of C(9)-protonated anthracene is at C(10).[9]

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