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AROMATIC PROTONATION—4[1]

ON THE ^1H–^2H EXCHANGE OF THREE 9-n-ALKYLANTHRACENES ON REACTION WITH $CF_3CO_2[^2H]$ AND $FSO_3[^2H]$

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Abstract—The reactions of 9-methyl-, 9-ethyl- and 9-propyl-anthracene with $CF_3CO_2[^2H]$ in $C[^2H]Cl_3$ and with $FSO_3[^2H]$ in SO_2ClF have been investigated. Using 4 equivalents of $CF_3CO_2[^2H]$ at 50° ^1H–^2H exchange was observed only for the 10-H and the side-chain α-hydrogens, and on using 8 and 12 equivalents at 50° also for the aromatic α-hydrogens. Treatment of the substrates with $FSO_3[^2H]$ at −60° leads to the stable 9-alkyl-[10-^2H]-10-anthracenium ions. On warming up to −25° a slow ^1H–^2H exchange of only the 10-^1H of these anthracenium ions is observed. A mechanism for the ^1H–^2H exchange of the aromatic and the side-chain α-hydrogens of the 9-alkylanthracenes is presented.

As an extension of our sulphonation studies on 9-n-alkylanthracenes[2] and in order to obtain more information on the Wheland intermediate formed by addition of SO_3 to the 10-position of these 9-alkylanthracenes,† we have studied the ^1H–^2H exchange of the three lowest members of the series of 9-n-alkylanthracenes. The hydrogen exchange of anthracene was studied before, illustrating the reactivity order to be 9-H ≫ 1-H > 2-H.[3] The only report on an alkylanthracene is the ^1H–^2H exchange of 9,10-dimethylanthracene in $CF_3CO_2[^2H]$.[4] From the incorporation of 12 ^2H atoms (determined mass spectrometrically) it was concluded that also the Me as well as the aromatic hydrogens undergo H-exchange. The H-exchange of the alkyl side chains of other aromatic substrates was also studied.[4,5] The suggested ^1H–^2H exchange of the β-hydrogens of hexaethylbenzene in $[^2H]_2SO_4$ in a mixture of $CF_3CO_2[^2H]$ and CCl_4 as solvent[4,5a] is questionable and invites to further study on the H-exchange of the n-alkyl side chain of aromatic hydrocarbons.

Reaction of toluene with 2 equivalents of $[^2H]F$–SbF_5 in SO_2ClF yields the 4-methyl-[1-^2H]-benzenium ion which does not exhibit any ^1H–^2H exchange of the Me hydrogens.[6]

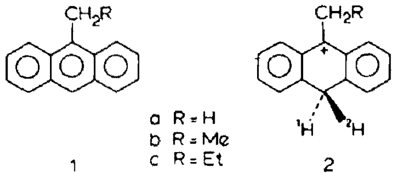
RESULTS

Reactions with $CF_3CO_2[^2H]$ *in* $C[^2H]Cl_3$. The ^1H NMR spectra of the reaction mixtures of **1a–1c** with $CF_3CO_2[^2H]$ in $C[^2H]Cl_3$ kept at 50° for the desired reaction time were recorded directly afterwards at *ca* 30°. From a comparison of these spectra with those of the 9-alkylanthracenes proper in $C[^2H]Cl_3$ (Table 1) it appeared (i) that the signals of *all* the aromatic and the side chain α-hydrogens were broadened, but not those of the side chain β- and γ-hydrogens, and (ii) that the intensity of some of the absorptions had been reduced, illustrating ^1H–^2H exchange. The number of ^2H-atoms incorporated at the several substrate positions are listed in Table 2. The content of total incorporated ^2H determined by ^1H NMR and FI mass spectrometry is the same within experimental error. The ^1H NMR spectrum of the 9-ethylanthracene isolated from the reaction mixture of **1b** with 12 equivalents of $CF_3CO_2[^2H]$ contains in addition to the triplet at δ 1.86 (J = 7.5 Hz) a doublet at δ 1.84 ppm (J = 7.5 Hz), whereas the methylene absorption at δ 4.03 shows a clean quartet (J = 7.5 Hz). These results clearly reveal the additional presence of the 9-$CH[^2H]CH_3$ group and thus the selective ^1H–^2H exchange of the α-hydrogens of the Et-group.

Reactions with $FSO_3[^2H]$ *in* SO_2ClF. Treatment of **1a–1c** with *ca* 20 equivalents of $FSO_3[^2H]$ in SO_2ClF as cosolvent at −60° leads to the stable 9-alkyl-[10-^2H]-10-anthracenium ions **2a–2c**, the ^1H NMR data of which are in Table 1. No ^1H–^2H exchange of any of the various hydrogens has been observed at this temperature within 30 min. On raising the temperature to −25° ^1H–^2H exchange but only of the 10-^1H of **2a–2c** was observed for 85 ± 10%.

DISCUSSION

The observed line broadening of all the aromatic hydrogens and the side chain α-hydrogens on treatment of the 9-alkylanthracenes with $CF_3CO_2[^2H]$ in $C[^2H]Cl_3$ may be explained in terms of the presence of a mixture of the substrate **1**, the Wheland intermediates **3–8** and the quinoid intermediates **9–11** in mutual equilibria (Scheme 1) which are rapid on the ^1H NMR time scale. Such an explanation would infer that all the hydrogens of which the signals are broadened would undergo ^1H–^2H



Scheme 1.

[†] This Wheland intermediate unexpectedly does not suffer loss of the 10-H proton with formation of the 10-sulphonic acid, but instead exhibits both sulphonation of the alkyl α-H and an intramolecular redox reaction with formation of 9-(alk-1-enyl)anthracene.[2]

Table 1. ^{1}H NMR data of the 9-alkylanthracenes **1** in C[^{2}H]Cl$_3$ and the 9-alkyl-[10-^{2}H]-10-anthracenium ions **2** in FSO$_3$[^{2}H] and SO$_2$ClF at −60°

Substrate	Chemical shifts (ppm) and multiplicities						
	1- and 8-H	4- and 5-H	2-,3-,6- and 7-H	10-H	Alkyl hydrogens		
					α	β	γ
1a	8.56(m)	8.28(m)	7.82(m)	8.68(s)	3.34(3H,s)		
1b	8.69(m)	8.39(m)	7.87(m)	8.69(s)	4.03(2H,q)[a]	1.85(3H,t)[a]	
1c	8.71(m)	8.39(m)	7.87(m)	8.70(s)	4.00(2H,t)	2.28(2H,sextet)[a]	1.55(3H,t)[a]
2a[b]	8.96(d)[c]	7.9-8.5(m)		5.09(bs)	3.76(3H,s)		
2b[b]	8.90(d)[c]	7.9-8.5(m)		5.09(bs)	4.15(2H,q)[a]	1.79(3H,t)[a]	
2c[b]	8.90(d)[c]	7.9-8.5(m)		5.08(bs)	4.12(2H,t)[a]	2.15(2H,sextet)[a]	1.44(3H,t)[a]

[a] J=7.5 Hz.

[b] The chemical shifts of these ions are almost equal to those of the corresponding non-deuterated 9-alkyl-10-anthracenium ions.[7]

[c] J=8.0 Hz.

Table 2. ^2H incorporation on reaction of 1a–1c with $CF_3CO_2[^2H]$ in $C[^2H]Cl_3$ at 50°[a]

			Number of incorporated ^2H atoms (± 5%)								
							Alkyl hydrogens			Total	
Substrate	Equiv. of $CF_3CO_2{}^2H$	Reaction time, h	1-,8- + 10-H	1- + 8-H[b]	4- + 5-H	2-,3-, 6- + 7-H	α	β	γ	^1H NMR	Mass spectral
1a	4	3	1.00		0.00	0.00[c]	0.89			1.89	
1a	8	17	1.16		0.16	0.00[c]	1.82			3.14	
1a	12	22	1.50	0.76	0.63	0.00[c]	2.11			4.24	
			(1.58)	(0.85)	(0.72)	(0.08)	(1.95)			(4.33)	(4.31)
1b	4	3	0.90		0.00	0.00[c]	0.17	0.00		1.07	
1b	8	17	1.15		0.11	0.00[c]	0.30	0.00		1.56	
1b	12	22	1.54	0.71	0.61	0.00[c]	0.38	0.00		2.53	
			(1.47)	(0.64)	(0.66)	(0.00)	(0.34)	(0.00)		(2.47)	(2.34)
1c	4	3	0.81		0.00	0.00[c]	0.26	0.00	0.00[c]	1.07	
1c	12	22	(1.51)	(0.69)	(0.78)	(0.08)	(0.23)	(0.00)	(0.00)[c]	(2.60)	(2.51)

[a] The data between brackets refer to the isolated 9-alkylanthracenes.

[b] The number of incorporated 1- and 8-^2H was calculated for the experiments with 12 equivalents of $CF_3CO_2[^2H]$ on the assumption that the ^1H-^2H exchange equilibrium for the 10-H and the acidic hydrogens had been completely established.

[c] These hydrogens were taken to undergo no ^1H-^2H exchange at all (see Experimental).

exchange which is in contrast with the observations for the 2-, 3-, 6- and 7-H (*cf* Table 2) and can therefore be ruled out. The line broadening is therefore ascribed to a fast degenerate electron exchange between the 9-alkylanthracene and its radical cation (of which the side chain α-carbon participates in the radical cationic character).[8]

The following ^1H–^2H exchange observations deserve discussion. With $CF_3CO_2[^2H]$ there is exchange of the side chain α-hydrogens, but not of the side chain β- and γ-hydrogens; there is exchange of the 10- and of the α-aryl hydrogens (the former being much faster than the latter), but not of the β-aryl hydrogens. With the highly acidic $FSO_3[^2H]$ at −60° only protonation at the 10-position takes place and no H-exchange, whereas at −25° a slow exchange, but only of the original 10-^1H, occurs.

The exchange of the aromatic hydrogens may be explained in terms of the occurrence of equilibrium I (Scheme 1), whereas the exchange of the side chain α-hydrogens is thought to proceed by the equilibria I -$1 \rightleftharpoons 7$) and II ($7 \rightleftharpoons 11$).† The latter sequence further illustrates the selective reactivity of the α-hydrogens of the side chain.

The equilibria I and II are similar to the ones proposed by Deno[9] (*cf* also Ref. [10]), Eaborn and Butler,[5b] and Stewart[5c] to explain the methyl H-exchange of hexamethylbenzene, some methyl substituted benzo[b]thiophens, and 2-amino-4-methylpyrimidine, respectively. The observations on the exchange of the side chain α-hydrogens of **1a–1c** with $CF_3CO_2[^2H]$ and $FSO_3[^2H]$ are in full agreement with the suggestion[4] that the exchange of these hydrogens can be observed only under certain defined conditions of acidity. At low acidities the content of the Wheland intermediate **7** is too small to lead to H-exchange (via **11**) at a reasonable rate. On the other hand at very high acidities the deuteration is virtually complete, but now the rate of detachment of the α-proton from the alkyl group of the Wheland intermediate **7** (leading to **11**) is very low in view of the extremely low basicity of the conjugate base A^-.

Taking into account the statistical factor, the rate of the H-exchange of the side chain α-hydrogen is very much greater for 9-methyl- than 9-ethyl- and 9-propylanthracene (Table 2). Two explanations may be considered. First, the equilibrium I ($1 \rightleftharpoons 7$) is more to the r.h.s. for 9-methyl than for the other two 9-alkylanthracenes. In fact, the basicity is somewhat greater for 9-methyl- than 9-ethyl-anthracene ($K_B = 10^{5.7}$ vs $10^{5.4}$ respectively).[11] Second, the equilibrium II ($7 \rightleftharpoons 11$) is more to the right for 9-methyl- than for 9-ethyl- and 9-propyl-anthracene due to a greater oppression between R and 1-H in **11** for R=Me and Et than for R=H. However, the strain energy of **11** is probably relieved in part through the adoption by the central ring of a flattened boat structure.‡

The number of incorporated ^2H atoms is very much greater for the α- than the β-aryl hydrogens (Table 2). This compares with the observed higher reactivity for the 1- than the 2-position of anthracene in the protiodetritiation in trifluoroacetic acid without solvent.[3b]

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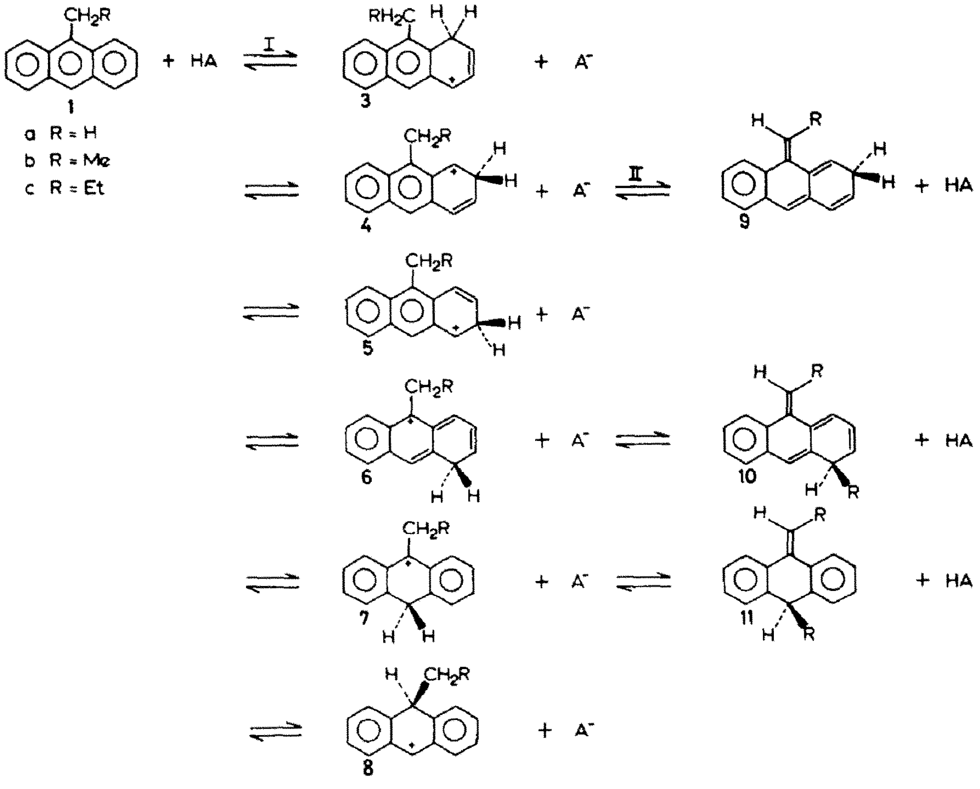
†The exclusive formation of the 9-alkyl-[10-^2H]-10-anthracenium ion in $FSO_3[^2H]$ in SO_2ClF at −60° indicates that the equilibria I ($1 \rightleftharpoons 4$ and $1 \rightleftharpoons 6$) in the $CF_3CO_2[^2H]$ system are relatively unimportant for the exchange of the α-hydrogens of the 9-alkyl group.

‡It was recently established that the central ring of 9-isopropylidene-10-alkyl-9,10-dihydroanthracenes has a butterfly, i.e. a flattened boat, conformation.[12]



Scheme 2.

The ^{2}H incorporation at the 1- and 8- and the 4- and 5-positions is comparable in magnitude. This illustrates that the free energy content of the Wheland intermediates **3** and **6** is about the same.

The implications of the present results as to the behaviour of the σ-complexes formed in the sulphonation of the 9-n-alkylanthracenes was discussed elsewhere.[2a]

EXPERIMENTAL

Materials. The preparation of 9-ethyl- and 9-propyl-anthracene was described.[2a] 9-Methylanthracene, FSO$_3$[^{2}H], SO$_2$ClF and CF$_3$CO$_2$[^{2}H] were commercially available reagents.

Reactions with CF$_3$CO$_2$[^{2}H]. To solns of 0.5 mmol of a given substrate in 1 ml C[^{2}H]Cl$_3$ were added at *ca* 20° in small portions 4 equivts (0.15 ml) of CF$_3$CO$_2$[^{2}H]. After heating the solns at 50° for 3 hr the ^{1}H NMR spectra were recorded at the probe temp (*ca* 30°). Immediately thereafter, an additional 4 or 8 equivts of CF$_3$CO$_2$[^{2}H] were added at *ca* 25°, the mixture heated at 50° for another 14 or 19 hr and the ^{1}H NMR spectra recorded again. With **1a** and **1b** this procedure was repeated once more using 4 equivts of acid and an additional heating at 50° of 5 hr. The 9-alkylanthracenes were isolated from the mixtures by adding a large excess of water, subsequent washing of the separated C[^{2}H]Cl$_3$ soln with water, NaHCO$_3$aq, and water, followed by drying over MgSO$_4$ and removal of the solvent.

Reactions with FSO$_3$[^{2}H]. The solns of the 9-alkyl-10-[^{2}H]-10-anthracenium ions were prepared by addition of *ca* 0.5 ml FSO$_3$[^{2}H] cooled at *ca* −78° to a cooled slurry of 0.5 mmol of the hydrocarbon in *ca* 0.5 ml SO$_2$ClF at −78°; the resulting mixtures were stirred vigorously until a clear soln was obtained.

Determination of ^{2}H *content of the various hydrogens.* The ^{2}H content of the various types of hydrogens of the substrates in the mixtures was calculated from the relative peak areas of the ^{1}H NMR absorptions of these hydrogens in the acidic mixtures, considering the absence of ^{1}H–^{2}H exchange of certain other hydrogens. For the mixtures of **1a**–**1c** with 4 equivts of CF$_3$CO$_2$[^{2}H], it was concluded that no ^{1}H–^{2}H exchange of the 2-H up to the 7-H had taken place, since the absorption area ratio of the 4- and 5-H over the 2-, 3-, 6- and 7-H remained 0.50 ± 0.01. For the mixture with 8 and 12 equivts of acid, it was assumed that no ^{1}H–^{2}H exchange of the β-aryl hydrogens had taken place. For the isolated **1c** it was assumed that no ^{1}H–^{2}H exchange of the γ-hydrogen of the side chain had occurred. The ^{2}H content of the various hydrogens of the isolated hydrocarbons was determined on the basis of the peak area ratios of the ^{1}H NMR absorptions and the total number of incorporated ^{2}H atoms, as determined by FI mass spectrometry.

^{1}H NMR *analysis.* The 100 MHz spectra were recorded with a Varian HA-100, equipped with a variable temperature probe. The chemical shifts are relative to external neat TMS (capillary).

FI *mass spectra.* The FI mass spectra were recorded on a Varian Mat 711 double focussing mass spectrometer equipped with a combined EI/FI/FD source. The FI measurements were obtained at a threshold of 10 nA and a direct insertion probe was used. It was checked using the unchanged substrates that under those conditions neither protonation nor loss of hydrogen took place.

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