Aromatic Sulphonation. Part 73.¹ Behaviour of Three 9-Alkylanthracenes containing One Side-chain α -Hydrogen in Dioxan–SO₃ Complex in Dioxan as Sulphonating Medium

By Freek van de Griendt and Hans Cerfontain,* Laboratory for Organic Chemistry, University of Amsterdam, Nieuwe Achtergracht 129, 1018 WS Amsterdam, The Netherlands

The reactions of 9-isopropyl-, 9-s-butyl-, and 9-cyclohexyl-anthracene with dioxan-SO₃ in dioxan at 17 °C lead to three types of products, *viz*. 9-alkenylanthracenes (2), unsaturated sulphonic acids (3), and seven-membered ring sultones (4). The 9-alkenylanthracenes (2) result from a redox reaction between the 9-alkylanthracenes and SO₃ and the unsaturated sulphonic acids (3) from the subsequent sulphonation of (2). The seven-membered ring sultones are formed from the σ -complex (resulting from addition of SO₃ to the 10-position of the original substrate) by a 1,2-hydride shift from the side-chain C- α to C-9.

THE reaction of 9-alkylanthracenes containing two sidechain α -hydrogens with dioxan-SO₃ leads, depending on the structure of the alkyl group, to α -alkylsulphonic acids and/or α -alkene- γ -sulphonic acids.¹ It was thought of

meric) products.[†] The reaction mixture of 9-isopropylanthracene (1a) with 1 equiv. dioxan-SO₃ after 20 min contained $45 \pm 3\%$ (1a), $17 \pm 3\%$ (2a), $29 \pm 3\%$ (3a'),[‡] *ca.* 2% (3a''), and $7 \pm 2\%$ (4a); this composition remained



SCHEME 1 Products obtained in the reactions of 9-isopropyl-,9-s-butyl-, and 9-cyclohexyl-anthracene with dioxan-SO₃

interest to study some 9-alkylanthracenes with a secondary side-chain α -carbon in order to determine the influence of the alkyl substituent at the side-chain α -carbon.

RESULTS

Reactions with Dioxan-SO₃.—9-Isopropyl- (1a), 9-sbutyl- (1b), and 9-cyclohexyl-anthracene (1c) were treated with $[{}^{2}H_{8}]$ dioxan-SO₃ complex in $[{}^{2}H_{8}]$ dioxan at 17 °C. The mixtures obtained with these substrates contained three types of reaction products (see Scheme 1), viz. 9alkenylanthracenes (2), unsaturated sulphonic acids (3), and seven-membered ring sultones (4), besides unchanged substrate and small amounts of unknown (probably polyconstant for a reaction time of at least 90 min. The reaction mixture of 9-s-butylanthracene (1b) with 1.5 equiv. dioxan–SO₃ after 20 min contained $45 \pm 3\%$ (1b), $18 \pm 2(32)\%$ § (2b), $8 \pm 2(15)\%$ (3b'), $8 \pm 2(15)\%$ (3b'), $12 \pm 2(23)\%$ (3b'''), and $8 \pm 2(15)\%$ (4b). After 45 min the composition of the mixture was found to be $22 \pm 2\%$ (1b), $25 \pm 2(32)\%$ (2b), $\| 16 \pm 2(20)\%$ (3b'), $\$ 12 \pm 2(16)\%$ (3b''), $17 \pm 2(22)\%$ (3b'''), $\| and 8 \pm 2(10)\%$ (4b).

The compositions of the reaction mixtures were determined by ¹H n.m.r. multicomponent analysis.³ The structural assignment of the compounds obtained from

 \parallel The configuration at the double bond could not be established in the absence of vinylic coupling. By analogy with the α ethylene- β -sulphonic acid and the α -alkene-y-sulphonic acids containing two vinylic hydrogens ¹ it is thought that (3b') and (3b''') have the *E*-configuration. Evidence in favour of this reasoning is the similarity in the chemical shift of the vinylic hydrogens of (3b''') and (3c) the latter of which has, in view of the cyclohexenyl structure, the *E*-configuration (see Table). On the basis of a similar comparison between the chemical shift of the vinylic hydrogens of (2b and c), it seems very likely that (2b) has the *E*-configuration.

 $[\]dagger$ In the reactions with $[{}^{1}\mathrm{H}_{8}]\mathrm{dioxan-SO}_{3}$ complex in $[{}^{1}\mathrm{H}_{8}]\mathrm{-}\mathrm{dioxan}$ no dioxan decomposition products were formed.²

 $[\]ddagger$ Product (3a') was proved ¹ to be a sulphonic acid by the i.r. absorptions of the corresponding sulphonate (in KBr) which are at 1 200 (s), 1 040 (m), and 730 (m) cm⁻¹.

[§] The data in parentheses give the relative product yields.

(1a and b) was based on their ¹H n.m.r. signals (see Table). The structure of (2a) was further proven by comparison of its spectrum with that of an independently synthesized sample.⁴ The structure of (4a) was assigned on the basis of its ¹H n.m.r. chemical shifts in comparison with those of the sultones formed in the reaction of 1-chloro- and 1,5-dichloro-9-isopropylanthracene with dioxan-SO₃.⁶ Further, the position of 10-H in (4a and b) (δ 5.74 and 5.75 respectively) is in agreement with that expected on the basis of the position of 9-H in 10-t-butyl-9,10-dihydroanthracene-9,10-sultone (δ 5.99).⁶ The structures of (2b), (3b'), (3b''), and (3b''') have further been proven by double resonance experiments.

The mixture of 9-cyclohexylanthracene (1c) with 1.5 equiv. dioxan-SO₃ after 20 min contained $50 \pm 5\%$ (1c), $15 \pm 3(30)\%$ (2c), $30 \pm 4(60)\%$ (3c), and $5 \pm 2(10)\%$ (4c). After 90 min the composition was: $41 \pm 5\%$ (1c), $13 \pm 3(21)\%$ (2c), $42 \pm 4(71)\%$ (3c), and $4 \pm 2(7)\%$ (4c). The structures of (2c) and (3c) are based only on the absorptions of β -H at δ 5.91 and 6.12 respectively which values are in good agreement with those obtained for the corresponding proton of (2a) (δ 5.89; the other vinylic hydrogen absorbs at δ 5.27) and (2b) (δ 6.28) for (2c), and of (3a) (δ 5.78 and 6.50) and (3b) (δ 5.92) for (3c). The assignment of the structure of (4c) is based on the positions of 9- and 10-H which are in good agreement with those of (4a and b).

The positively assigned 1 H n.m.r. data of all the reported compounds are listed in the Table.

the preceding paper for the formation of the 9-alkenylanthracene, proposed as an intermediate in the reaction of the 9-alkylanthracenes, containing two side-chain α -hydrogens, with dioxan-SO₃.¹

Product (4) is formed by the steps (1), (4), and (5). Step (4) represents a 1,2-hydride shift from the sidechain α -carbon to C-9. A related 1,2-methyl shift, but with $[{}^{2}H_{6}]$ dimethyl sulphoxide as solvent, was reported for the rearrangement of 10-t-butyl-9,10-dihydroanthracene-9,10-sultone into 9-methyl-9-(prop-2-enyl)-9,10-dihydroanthracene-10-sulphonic acid.⁶ Ring closure of the resulting dipolar structure then yields the sultone (4) [step (5)].

In the σ -complex (I) there exists, in view of the planarity at the sp^2 C-9 atom, steric repulsion between the alkyl side-chain and 1- and 8-H on the one hand, and of the sulphonate group and 4- and 5-H on the other. Both steps (2) and (4) are accompanied by relief of the steric strain, as the central ring of (II) will have a *cis* ' boat ' or ' butterfly ' structure as in 9-isopropylidene-10-isopropyl-9,10-dihydroanthracene,⁷ and that of (III) a non-planar boat structure similar to that of 9,10-dialkyl-9,10-dihydroanthracene.⁸

The only difference between the reactions of 9-alkylanthracenes containing two side-chain α -hydrogens ¹ and

¹H N.m.r. data of the substrates and products in [²H₈]dioxan

Compound	Ö					
	a-H ª	β-H ª	γ-H ⁴	α'-H ª	9-H ^ø	10-Н 🖉
(la)	4.77 (1 H, m)	1.87 (3 H, d)		1.87 (3 H, d)		8.50 (s)
ùы́	4.49 (1 H. m)	2.37 (2 H, m)	0.99 (3 H, t)	1.85 (3 H, d)		8.52 (s)
(1c)	4.29 (1 H, t)					8.43 (s)
(2a)		5.27 (1 H, s)		2.37 (3 H, s)		8.50 (s)
(2b)		6.28 (1 H, q)	1.41 (3 H, d)	2.33 (3 H, s)		ca. 8.6 (s)
(3a')		5.78 (1 H, s)		4.59 (2 H, s)		8.60 (s)
(3a'')		6.86 (1 H, s)		2.81 (3 H, s)		
(3b')		6.86 (1 H, q)	1.55 (3, H, d)	5.22 (2 H, s)		8.61 (s)
(3b'')		ca. 4.5	1.94 (3 H, d)	5.85 (1 H, s) 6.64 (1 H, s)		8.61 (s)
(3b''')		5.92 (1 H, t)	ca. 4.5	2.45 (3 H, s)		8.61 (s)
(3c)		6.12 (d)		(, ,		8.55 (s)
(4a)		1.53 (3 H. s)		1.53 (3 H, s)	4.10 (1 H, s) °	5.74 (1 H, s) °
(4b)		ca. 2.2	ca. 1.1	1.48 (3 H, s)	4.15 (1 H, s) °	5.75 (1 H, s) °
(4c)				, ,	3.99 (1 H. s)	5.68 (1 H, s) °

^a α , β , *etc.* refers to the side-chain carbon. These carbons are numbered according to: $\alpha'C-(C^{\alpha}-Ar)-C^{\beta}-C^{\gamma}$. Further with (2a), (3a'), and (3a'') β -C represents the double bonded carbon. The side-chain hydrogens other than those specificially listed yield for (1c) a multiplet at δ 1.9–2.7, and for (2c) and (3c) a multiplet at δ 1.5–2.6. ^b 2-, 3-, 6-, 7-H of all the anthracene derivatives give a multiplet of total width of *ca.* 15 Hz, centred at δ 7.60 \pm 0.05, and 4- and 5-H a *ca.* 15 Hz multiplet centred at δ 8.14 \pm 0.05. 1- and 8-H exhibit a *ca.* 15 Hz multiplet centred for the substrates at δ 8.65 \pm 0.05, for (2a) at δ 8.27, for (3a') at δ 8.39, for (2b) and (3b', b'', and b'') at δ 8.19 and for (3c) at δ 8.13 and 8.31. ^e 9- and 10-H of the sultones represent the hydrogens attached to the central ring, at the side of the alkyl group and the SO₂ group, respectively.

DISCUSSION

The reaction of the three investigated substrates with dioxan-SO₃ yields 9-alkenylanthracenes (2), unsaturated sulphonic acids (3), and seven-membered ring sultones (4). The formation of (2) and (4) may be explained as depicted in Scheme 2 for 9-isopropylanthracene. The unsaturated sulphonic acids are thought to result from the sulphonation of the unsaturated hydrocarbons (2).

The formation of (2) may be explained in terms of steps (1)—(3) which are identical to those suggested in

9-isopropyl-, 9-s-butyl-, and 9-cyclohexyl-anthracene with dioxan–SO₃ complex is the formation of the sultones (4) with the latter series of substrates. The absence of sultone formation with the former substrates may be due to the improbability of the hydride shift [step (4)] which would yield a secondary carbenium ion which is less stable than the preceding ' tertiary ' one.

Evidence in favour of the presumed intermediacy of 9-alkenylanthracenes (2) in the formation of the unsaturated sulphonic acids (3) is (i) the formation of



SCHEME 2

(3a') and (3a'') from both neat 9-isopropylanthracene (1a) and neat 9-(prop-2-enyl)anthracene (2a) and (ii) the smaller amount of SO₃ required for the latter as compared with the former substrate. Sulphonation of (2a) In the reaction of the 9-alkylanthracenes, containing two side-chain α -hydrogens, no 9-alkenylanthracenes have been detected. The presence of (2a) in the reaction of 9-isopropylanthracene indicates that sulphonation of (2a) is slower than that of the 9-alkenylanthracenes resulting from the other 9-alkylanthracenes under discussion.

The formation of the products (2b), (3b'), (3b''), and (3b''') from 9-s-butylanthracene may be explained as depicted in Scheme 4. In the redox reaction of SO₃ with 9-s-butylanthracene two 9-alkenylanthracenes, viz. (2b) and (2b'), may be formed [overall steps (6) and (7) respectively]. The unsaturated hydrocarbon (2b') is proposed as intermediate in the formation of (3b'), and (2b) in that of (3b'') and (3b'''). In view of their relative energy contents it is to be expected that (2b) is formed in greater amounts than (2b'). This is in fact observed as for a reaction time of 45 min the sum of (3b') and (2b') (which intermediate is not present beyond the limits of its ¹H n.m.r. detection) is $(16 + \leq 3)$ % and the sum of (2b), (3b"), and (3b") 54%. The sulphonic acids (3b' and b'') are the homologues of (3a'), which is obtained in the sulphonation of (2a) (see Scheme 3), whereas (3b''') is the homologue of the α -alkene- γ sulphonic acid obtained in the reaction of e.g. 9-propylanthracene with dioxan-SO₃.¹

The reactions of 9-alkylanthracenes containing two side-chain α -hydrogens yield products with an α -alkene- γ -sulphonic acid side-chain structure which were proposed to be formed via 9-(alk-1-enyl)anthracene as intermediates.¹ With that type of substrate these intermediates could not be detected, but now they have been observed with 9-s-butyl- and 9-cyclohexyl-anthracene. The presence of observable concentrations of (2b and c) respectively may be related to the lower degree or absence of the alkenyl hyperconjugative stabilization of the σ complex resulting on SO₃ addition to the 10-position of the 9-alkenylanthracene which infers a lower acidity of the γ -hydrogens [cf. (IV) in Scheme 2 of the preceding paper ¹], due to additional steric inhibition from the presence of the added alkyl group at the α -carbon. This



with dioxan-SO₃ does not yield (4a) illustrating that this product is formed directly from 9-isopropylanthracene. The sulphonation of (2a) leads to (3a') as the main product. Its formation is proposed to proceed as

* A general and extensive discussion on the side-chain sulphonation of some 9-alkenylanthracenes in relation to that of the corresponding alkenylbenzenes is given in the following paper.⁴ will reduce the rate of γ -sulphonation [step (9) in Scheme 2 of the preceding paper ¹]. From molecular models it appears that the additional α -alkyl group does prevent the C- α -C- β -double bond from being planar with the anthracene ring.[†]

 \dagger For comparison the dihedral angle between the planes of the two aryl groups of 9-phenylanthracene is $67^{\circ,9}$

The low rate of sulphonation of (2b and c) is not only apparent from the detection of these intermediates in the reaction of (1b and c), respectively, but that of (2c) also from the change in composition of the reaction mixture of



9-cyclohexylanthracene with time [the ratio of (2c) to (3c) after 20 and 90 min being 0.50 and 0.30, respectively].

The reaction of 9-cyclohexylanthracene with dioxan-SO₃ yields only the α -alkene- γ -sulphonic acid (2b). The absence of products homologous with (3a', a'', b', and b'') is probably due to the steric interaction between the side-chain and 1- and 8-H.

EXPERIMENTAL

Materials.—The three 9-alkylanthracenes have been synthesized by reaction of anthrone with a three-fold excess

of the appropriate Grignard reagent.¹⁰ 9-Hydroxy-9-isopropyl-9,10-dihydroanthracene was found to dehydrate under the reaction conditions with formation of the desired 9-isopropylanthracene, but in reactions leading to 9-s-butyland 9-cyclohexyl-anthracene the 9-alkyl-9-hydroxy-9,10dihydroanthracenes were obtained as such (cf. ref. 11). The dihydroanthracenes were purified by chromatography on neutral alumina (eluant benzene), followed by recrystallization from light petroleum (b.p. 40–60°). They (0.04 mol) were dehydrated by heating them with phosphorus pentaoxide (0.07 mol) in carbon tetrachloride (150 ml) at 70 °C for 2 h.^{11b} The solution was decanted, washed with water, and dried (MgSO₄). 9-Alkylanthracenes were purified as described before.¹

Reaction Procedures.—The reactions with dioxan– SO_3 complex have been carried out as described before,¹ using variable amounts of SO_3 .

Spectral Analysis.—¹H N.m.r. spectra were recorded with a Varian HA-100 or XL-100 spectrometer; chemical shifts (δ) are relative to external tetramethylsilane (capillary). I.r. spectra (KBr) were recorded with a Perkin-Elmer 177 spectrometer.

[8/1959 Received, 10th November, 1978]

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