Isomerization and Sulfodeprotonation in the Reaction of 1,6-Oxido[10]annulene, 1,6-Imino[10]annulene, Their Isomers 1-Naphthol and 1-Aminonaphthalene, and 11-Oxo-1,6-methano[10]annulene with SO_3†

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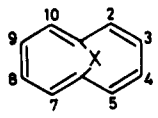
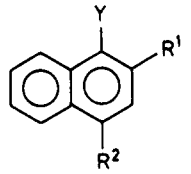
The reactions of 1-naphthol (**3**), 1-aminonaphthalene (**10**), and 1,6-oxido- (**1**), 1,6-imino- (**2**), and 11-oxo-1,6-methano[10]annulene (**15**) with SO_3 in aprotic solvents have been studied. With **3** the initial product is 1-naphthyl hydrogen sulfate (**4**), which is slowly converted into the 1-naphthol-2- (**5**) and -4-sulfonic acid (**6**) via O-desulfonation and C-sulfonation on using ≤1 equiv of SO_3, but via C-sulfonation and O-desulfonation if the SO_3 is in a large excess. It is suggested that on using ≤1 equiv of SO_3 the conversion of **4** into the 2-sulfonic acid **5** proceeds intramolecularly. The annulene **1** with SO_3 in dioxane initially yields 1-naphthol and its hydrogen sulfate (**4**), which at temperatures >−30 °C undergo ring sulfonation (vide supra). The nitrogen-containing substrates behave quite similarly to their oxygen analogues in that both **10** and **2** yield **10**-2-SO_3H, **10**-4-SO_3H, and **10**-2,4-$(SO_3H)_2$. With **2**, the initial product is the *N*-sulfonic acid **9**. The ketone **15** undergoes ring substition with formation of the 2-sulfonic and 2,7-disulfonic acids. Mechanisms have been presented to rationalize the skeletal rearrangements of the annulenes **1** and **2**.

In continuation of our studies on the spectroscopy[1] and chemistry[2-5] of bridged [10]annulenes, we now report on the reactions of 1,6-oxido- (**1**), 1,6-imino- (**2**), and 11-oxo-1,6-methano[10]annulene (**15**) with SO_3 in dioxane. In view of the products resulting from **1** and **2** we have also studied the sulfonation of the isomeric 1-naphthol (**3**) and 1-aminonaphthalene (**10**) The first synthesis of **1** was





1 X = O
2 X = NH
9 X = NSO_3H
15 X = C=O

3 Y = OH ; $R^1 = R^2 = H$
4 Y = OSO_3H ; $R^1 = R^2 = H$
5 Y = OH ; $R^1 = SO_3H$; $R^2 = H$
6 Y = OH ; $R^1 = H$; $R^2 = SO_3H$
7 Y = OSO_3H ; $R^1 = H$; $R^2 = SO_3H$
8 Y = OH ; $R^1 = R^2 = SO_3H$
10 Y = NH_2 ; $R^1 = R^2 = H$
11 Y = $NHSO_3H$; $R^1 = R^2 = H$
12 Y = NH_2 ; $R^1 = SO_3H$; $R^2 = H$
13 Y = NH_2 ; $R^1 = H$; $R^2 = SO_3H$
14 Y = NH_2 ; $R^1 = R^2 = SO_3H$

reported by Sondheimer.[6] On studying the chemistry he observed that **1** in the presence of Lewis acids like BF_3 or silica gel is converted into 1-benzoxepin and 1-naphthol, but that in the presence of aqueous acetic acid 1-benzoxepin, and 1- and 2-naphthol are formed in a 1:1:1 ratio.[6] Attempted sulfonation of **1** with fuming sulfuric acid in dioxane at room temperature indicated the formation of naphthalene derivatives, although no pure substance could be isolated.[6]

Results

The reactions of the aromatic substrates with SO_3 were mainly studied in ($^2H_8$)dioxane as the solvent, or in a mixture of ($^2H_8$)dioxane and ($^2H_2$)methylene chloride when the desired reaction temperature was below the dioxane melting point. The ^1H and ^{13}C NMR assignments of the substrates[7] and the sulfonic acid products are compiled in Tables I–III (supplementary material). The compositions of the sulfonic acid product mixtures were determined by ^1H NMR multicomponent analysis on the basis of the specific absorption(s) of the various components.[8]

1,6-Oxido[10]annulene (1). The homogeneous reaction of **1** with 1–5 equiv of SO_3 in dioxane (in the presence of methylene chloride as cosolvent or not) leads to the formation of 1-naphthol and its sulfation and sulfonation products (Table IV). When 1.0 equiv of SO_3 at −60 °C (cf. Figure 1) is used, the main initial products are 1-naphthyl hydrogen sulfate (**4**) and 1-naphthol (**3**) formed in a 2:1 ratio and in addition some 1-naphthol-2- (**5**) and -4-sulfonic acid (**6**).[9] When the temperature is raised, the amount of the latter two acids and **3** increase at the expense of the 1,6-oxido[10]annulene (**1**). The ratio of **5** to **6** is 2.0 ± 0.2. At temperatures <−40 °C the 1-naphthyl hydrogen sulfate (**4**) is relatively stable; at higher temperatures it is converted to yield 1-naphthol (**3**) and its 2- (**5**) and 4-sulfonic acid (**6**). When 2.0 equiv of SO_3 at 15 °C is used, the 4-sulfo-1-naphthyl hydrogen sulfate (**7**), initially present for 19%, disappears to form the 1-naphthol-4-sulfonic acid (**6**). The eventual product is 1-naphthol-2,4-disulfonic acid which is in fact formed in 90% yield on using 5.0 equiv of SO_3. The **5**/(**6** + **7**) ratio appears to be constant, with a value of 0.9 ± 0.1, independent of the **6**/**7** ratio. Apparently **7** is the precursor

† Aromatic Sulfonation. 97. For part 96, see: Cerfontain, H. *Recl. Trav. Chim. Pays-Bas* **1985**, *104*, 153.

(1) Andrea, R. A.; Cerfontain, H.; Lambrechts, H. J. A.; Louwen, J. N.; Oskam, A. *J. Am. Chem. Soc.* **1984**, *106*, 2531.
(2) Lammertsma, K.; Cerfontain, H. *J. Am. Chem. Soc.* **1978**, *100*, 8244.
(3) Lambrechts, H. J. A.; Cerfontain, H. *Recl. Trav. Chim. Pays-Bas* **1981**, *100*, 291.
(4) Cerfontain, H.; Goossens, H.; Koeberg-Telder, A.; Kruk, C.; Lambrechts, H. J. A. *J. Org. Chem.* **1984**, *49*, 3097.
(5) (a) Lammertsma, K.; Cerfontain, H. *J. Am. Chem. Soc.* **1980**, *102*, 3257; (b) *Ibid* **1980**, *102*, 4528.
(6) Shani, A.; Sondheimer, F. *J. Am. Chem. Soc.* **1967**, *89*, 6310.
(7) The ^1H NMR data of **1** were reported before. See Günther, A. *Z. Naturforschung.* **1965**, *20b*, 948.
(8) Cerfontain, H.; Koeberg-Telder, A.; Kruk, C.; Ris, C. *Anal. Chem.* **1974**, *46*, 72.
(9) The chemical shifts of the 15% of **1** present in the reaction mixture using 1.0 equiv of SO_3 in ($^2H_8$)dioxane/($^2H_2$)methylene chloride (1:5 v/v) at −60 to −40 °C are the same as those of **1** proper in the same mixture, viz. 7.68 and 7.44 vs. 7.67 and 7.43 ppm, respectively. Apparently the degree of complexation of the nonconverted **1** by the residual SO_3 is at most small.

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Table IV. Reaction of 1,6-Oxido[10]annulene (1) with SO_3 in Dioxane

reaction conditions				reaction mixture composition, % ± 3								
SO_3 equiv	solvent[a]	temp, °C	reactn time, ks	1	3	4	5	6	7	8	unidentified product(s)	5/(6 + 7)
1.0	D-d_8/MC-d_2[b]	−60	0.9	15	19	40	← 5 →				21	
		−50	2.8	15	20	39	← 5 →				21	
		−40	3.5	15	21	35	← 7 →				22	
		−30	4.8	9	27	33	← 10 →				21	
		−20	5.5	6	28	35	← 11 →				20	
		−10	8.0	<1	29	30	10	5			26	2.0
			9.3		28	26	12	7			27	1.7
			11.8		32	13	17	9			29	1.9
		0	14.0		33	4	22	11			30	2.0
		10	15.1		36	<1	23	11			30	2.1
		15	18.7		33		24	11			32	2.2
		25	90		30		25	12			33	2.1
2.0	D-d_8	15	0.8				27	16	19	13	25	0.8
			1.2				32	19	15	18	16	0.9
			1.8				35	20	13	20	12	1.1
			3.0				31	25	9	28	7	0.9
			5.4				28	28	4	31	9	0.9
			12.6				28	30	<1	33	9	0.9
			90				27	29		36	8	0.9
5.0	D-d_8	35	10.8							90	10	

[a] D-d_8 and D-d_8/MC-d_2 stand for ($^2H_8$)dioxane and ($^2H_8$)dioxane/($^2H_2$)methylene chloride (1:5 v/v), respectively. [b] The reaction with 1.0 equiv of SO_3 (0.20 mmol) was executed in a mixture of 2.2 mmol of D-d_8 and 15.3 mmol of MC-d_2.

Table V. Reaction of 1-Naphthol (3) with SO_3

reaction conditions				reaction mixture composition, % ± 2						
SO_3 equiv	solvent[a]	temp, °C	reactn time, ks	3	4	5	6	7	8	5/(6 + 7)
0.7[a]	D-d_8/MC-d_2	0	10.8	45		35	20			1.8
1.1	D-d_8/MC-d_2	−60	1.1		100					
		−40	2.4		100					
		−30	2.9		≥98	← ≤2 →				
		−20	3.5		92	5	3			1.7
		−10	4.0		80	13	7			1.9
		0	4.7		52	31	17			1.8
			5.2		31	44	25			1.8
			5.8		16	54	30			1.8
			9.0		<1	63	37			1.7
			10.2			63	37			1.7
2.0	D-d_8	15	0.6		6	17	63	8	6	0.24
			1.5		4	17	63	8	8	0.24
			2.4		3	18	66	3	10	0.26
			9.3		1	19	68	<1	12	0.28
			80			17	69		14	0.25
2.0	D-d_8	35	10.8			16	71		13	0.23
1.0	N	0	14.4	≤1		15	85			0.18
4.0	N	0	14.4	<1					>99	

[a] D-d_8, D-d_8/MC-d_2, and N stand for ($^2H_2$)dioxane, solvent mixture of ($^2H_8$)dioxane and ($^2H_2$)methylene chloride (1:5, v/v), and nitromethane, respectively.

of **6**. It is striking that the **5**/(**6** + **7**) ratio is significantly smaller on using 2.0 rather than 1.0 equiv of SO_3, viz., 0.9 vs. 2.0. On reaction of **1** with SO_3 there is not observed any 1,6-oxido[10]annulene-2-sulfonic acid.[10] For this acid would have revealed itself by the low-field ^1H NMR doublets of H(3) and H(10).[11]

1-Naphthol (3). The homogeneous sulfonation of **3** with SO_3 in dioxane—in the presence of methylene chloride as cosolvent or not—leads to the sulfation and sulfonation products **4**–**8** (Table V). On using ≤1.1 equiv of SO_3, there is no 4-sulfo-1-naphthyl hydrogen sulfate (**7**) present. The **5**/**6** ratio is equal to 1.8 ± 0.2, independent of both the temperature and the 1-naphthyl hydrogen sulfate (**4**) to the 1-naphthol monosulfonic acid (**5** + **6**) ratio. When 2.0 equiv of SO_3 is used, **7** and **8** are additional products; the **5**/(**6** + **7**) ratio is now very significantly smaller (0.24) than for the experiments using 0.7 and 1.1 equiv of SO_3 (1.8).

It is striking that the reaction of 1-naphthol with ≤1.1 equiv of SO_3 in dioxane as solvent leads mainly to the 2-sulfonic acid, whereas the predominant product on using nitromethane as solvent is the 4-sulfonic acid.

1,6-Imino[10]annulene (2) and 1-Aminonaphthalene (10). The reactions of **2** with 1–5 equiv of SO_3 in ($^2H_8$)-dioxane are all heterogeneous and lead ultimately to the sulfonation products of **10**. The heterogeneous mixture obtained on reaction of **2** with 1.0 equiv of SO_3 in ($^2H_8$)-dioxane after stirring for 20 min at 35 °C contains only the sulfamate **9**. This was concluded from the lower field absorption of the two ^1H NMR AA'BB' multiplets, observed for the homogeneous solution obtained by adding 20 vol % of ($^2H_2$)water to a small sample taken from the heterogeneous reaction mixture, as compared with those of **2** proper in the same solvent mixture, the two multiplets

(10) Our tentative conclusion that 1,6-oxido[10]annulene on reaction with SO_3 would yield 1,6-oxido[10]annulene-2-sulfonic acid (ref 9 in: Andrêa, R. R.; Cerfontain, H.; Lambrechts, H. J. A.; Louwen, J. N.; Oskam, A. *J. Am. Chem. Soc.* **1984**, *106*, 2531) thus appears to be erroneous.

(11) The ^1H NMR absorption of H(3) and H(10) of 1-2-SO_3H would have been shifted downfield relative to those of 1 by 0.4 and 0.6 ppm, respectively, due to the $-SO_3H$ substituent shift (cf. Table I of ref 4).

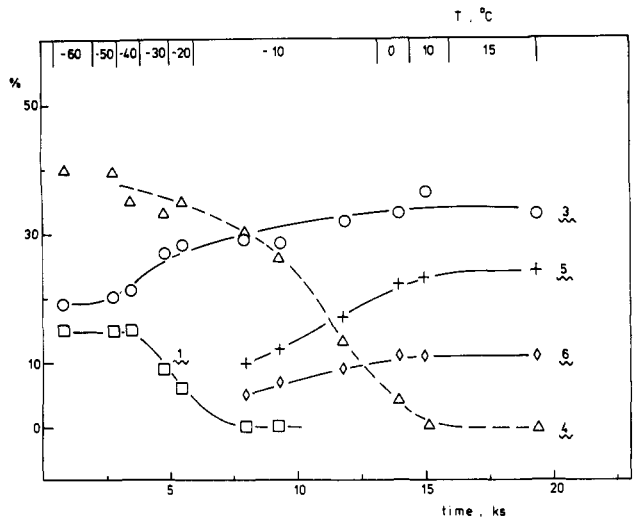


Figure 1. Reaction of 1,6-oxido[10]annulene (1) with 1.0 equiv of SO_3 in ($^2H_8$)dioxane + ($^2H_8$)methylene chloride at −60 to 15 °C; variation of product composition with temperature and reaction time.

being centered at 8.07 and 7.81 vs. 7.72 and 7.37 ppm, respectively. The slow decomposition of the observed entity in this acidic aqueous dioxane solution with initial reformation of **2**,[12] as established by ^1H NMR, is in line with the proposed initial formation of the sulfamate **9**. After a total stirring of 4 h, the reaction mixture was worked up (see Experimental Section) and the resulting freeze-dried material found to contain 10% of **2** (probably formed from **9** during the work-up procedure), 12% of 1-aminonaphthalene (**10**), and 4% of both its 4-sulfonate and 2,4-disulfonate (**14**). Upon using ≥2.0 equiv of SO_3 the main product is 1-aminonaphthalene-2,4-disulfonic acid (**14**).

The heterogeneous reaction of 1-aminonaphthalene (**10**) with 1.0 equiv of SO_3 in dioxane after stirring for 4 h at 35 °C yields the 2- (**12**) and 4-sulfonic acid (**13**) (29% of each) in addition to the 2,4-disulfonic acid (**14**) (13%).

11-Oxo-1,6-methano[10]annulene (15). The homogeneous reaction of **15** with 5 equiv of SO_3 in ($^2H_8$)dioxane at 35 °C for 3 and 24 h leads to sulfodeprotonation with formation of the 2-sulfonic acid as the only product in yield of 87 and >99%, respectively. The homogeneous reaction of **15** with 5 equiv of SO_3 in CH_3NO_2 at 35 °C for 3 h yields 40% 2,7-disulfonic acid in addition to other (as yet unassigned) products.

Discussion

1-Naphthol. The initial reaction of 1-naphthol (**3**) with SO_3 in an aprotic solvent is sulfation with formation of 1-naphthyl hydrogen sulfate (**4**) (cf. Table V) in an equilibrium reaction which is far to the side of **4**. The subsequent formation of the 1-naphthol-2- and -4-sulfonic acids may proceed from the aryl hydrogen sulfate via two routes:[13] first, using a deficient amount of SO_3 realtive to the amount of 1-naphthol, by a relatively slow regeneration of 1-naphthol and SO_3 and subsequent ring sulfonation; second, using an excess of SO_3 relative to the initial amount of 1-naphthol, additionally by initial C-sulfodeprotonation of the aryl hydrogen sulfate and subsequent O-protodesulfonation. In fact, the variations in the yields of **6** and **7** in the series of experiments using 2.0 equiv of SO_3 in dioxane (Table V) clearly illustrate that **6** is formed (at least in part) via **7** as the intermediate.

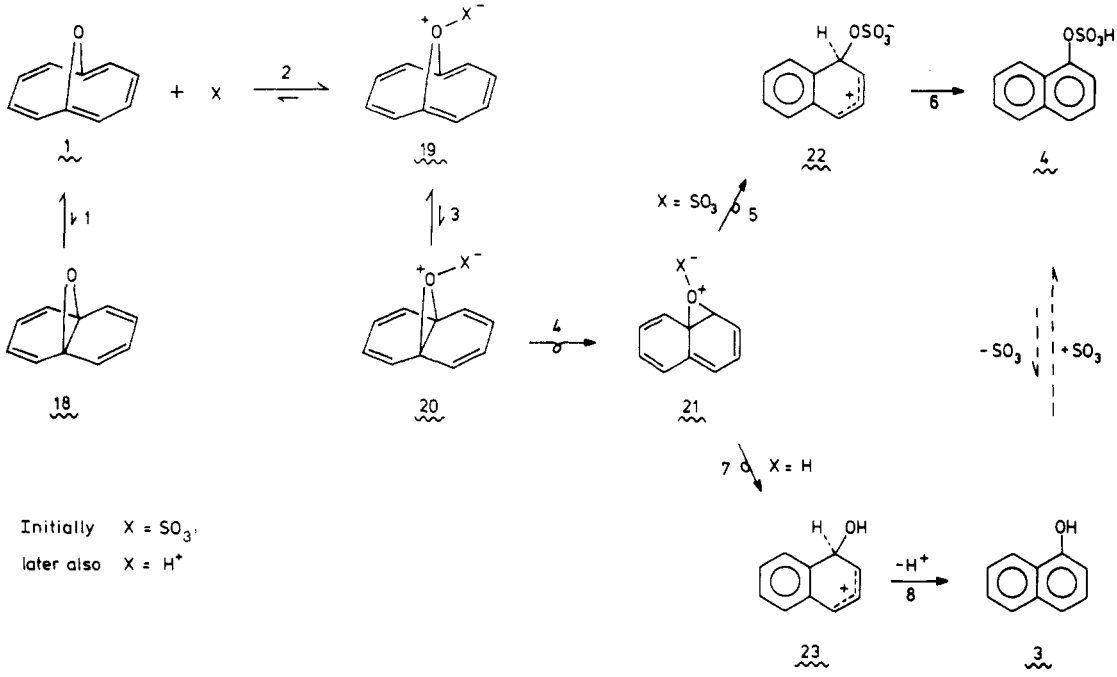
The ratio of the 2- to 4-sulfonic acid is significantly greater on using ≤1.1 than 2.0 equiv of SO_3 (1.8 vs. 0.24). The high f_2/f_4 partial rate factor ratio is ascribed to sulfonation of the 1-naphthol via O-desulfonation and C-sulfonation, whereas the low ratio is thought to result from the (additional) sulfonation of the 1-naphthyl hydrogen sulfate (**4**), followed by O-desulfonation. The much lower f_2/f_4 ratio for the latter reaction sequence is ascribed to steric hindrance for the 2-substitution by the $-OSO_3H$ substituent of which the SO_3H group points away from C(8).[14,15] When ≤1.0 equiv of SO_3 in nitromethane at 0 °C is used, the f_2/f_4 ratio is much greater for 1-naphthol (0.18) than for phenol[16] (≤0.01[13]). This observation is remarkable, since the sulfonation of naphthalene with SO_3 in nitromethane at 0 °C is slower for the β- than the α-position, f_2/f_1 being 0.14.[18] It has been proposed that the regeneration of SO_3 from phenyl hydrogen sulfate proceeds by an A-1 mechanism and that the isomerization of phenyl hydrogen sulfate to phenol-4-sulfonic acid proceeds intermolecularly.[13,19] It may therefore well be that the conversion of 1-naphthyl hydrogen sulfate (**4**) into 1-naphthyl-2-sulfonic acid (**5**) proceeds intramolecularly, especially since the C(1)–C(2) bond length is somewhat less in naphthalene than benzene (1.371 vs. 1.397 Å).[20]

The f_2/f_4 ratio for the sulfonation of 1-naphthol with 1 equiv of SO_3 is very much greater for dioxane than nitromethane as solvent (1.8[21] vs. 0.18). This is ascribed to a specific solvation of the intermediates **16** and **17** for the intramolecular isomerization by a solvent molecule in the case of dioxane as solvent, (cf. Scheme I, supplementary material), leading to a rate enhancement for the 2- as compared with the 4-substitution for that solvent.[21]

1,6-Oxido[10]annulene. The reaction of **1** with SO_3 in dioxane leads to the formation of six identified products, viz., **3**–**8**. At temperatures below −50 °C the main products are 1-naphthol (**3**) and its hydrogen sulfate (**4**), the amounts of 1-naphthol-2- and -4-sulfonic acid being rela-

(12) Benson, G. A.; Spillane, W. J. *Chem. Rev.* **1980**, *80*, 151.
(13) Cerfontain, H.; Koeberg-Telder, A.; Lambrechts, H. J. A.; de Wit, P. *J. Org. Chem.* **1984**, *49*, 4917.
(14) For optimum conjugation between the hydrogen sulfate and the 1-naphthyl moieties of **4**, the torsional angle around the C(1)–O bond should be minimal, viz., $\varphi = 0°$ [i.e. with the $-SO_3H$ group pointing away from C(8)] or 180°. From studies with Catalin Stuart molecular models it appears that steric hindrance by H(2) and H(8) induce torsion around the C(1)–O bond with $\varphi = 27$ and 115°, respectively. The conformer with the former torsion angle is the more stable one, as the deviation from the coplanar structure is less with the former than the latter, $\Delta\varphi$ being 27 vs. 65°, respectively.
(15) In accordance, 1-naphthyl methanesulfonate (an aprotic analogue of **4**) upon sulfonation with 4 equiv of SO_3 in nitromethane at 0 °C yields exclusively the 4-sulfonic acid [^1H NMR of the potassium sulfonate in [$^2H_2$]O (δ, ppm): H(2) 7.86 (d); H(3) 8.55 (d); H(5) 9.08 (d,d); H(6) 8.17 (t, d); H(7) 8.01 (t, d); H(8) 8.45 (d, d); Me 3.82 (s); all $^3J_{ortho} \simeq 8$ and $^4J_{meta} \simeq 1.5$ Hz], de Wit, P.; Cerfontain, H., to be published.
(16) Phenol on reaction with 1.0 equiv of SO_3 in dioxane at 17 °C yields only phenyl hydrogen sulfate which product remains stable for at least three days and does not undergo ring substitution.[17]
(17) Goossens, H.; Lambrechts, H. J. A.; Cerfontain, H., unpublished results; Suter, C. M.; Evans, P. B.; Kiefer, J. M. *J. Am. Chem. Soc.* **1938**, *60*, 538.
(18) The formation of small amounts of the 1-naphtholmonosulfonic acids **5** and **6** from **1** at −60 °C is remarkable, since 1-naphthol at that temperature does not yield these compounds (Tables IV and V). It may be due to some local overheating during the addition of the neat SO_3 to the reaction mixture of **1**, especially since it is known that the 1,6-methano[10]annulene system is far more reactive than the naphthalene system.[4]
(19) Kice, J. L.; Anderson, J. M. *J. Am. Chem. Soc.* **1966**, *88*, 5242.
(20) Herndon, W. C. *J. Am. Chem. Soc.* **1974**, *96*, 7605.
(21) When not fully dry dioxane is used, the **5**/**6** ratio is still higher, the observed values on using 1.0 and 2.0 equiv of SO_3 being 3.8 and 1.3, respectively.[22] Possibly the negative charges of the $-SO_3^-$ group of **16** and **17** are solvated by the strong Brønsted acids $H_2S_2O_7$, $H_2S_3O_{10}$, and $H_2S_4O_{13}$[23] (formed on addition of SO_3 to the slightly aqueous dioxane), rendering the sulfur atom of **16** more electron deficient and thus more prone to migrate to C(2).
(22) Goossens, H.; Koeberg-Telder, A., unpublished results.
(23) Stopperka, K.; Neumann, V. A. *Z. Anorg. Allg. Chem.* **374**, *1970*, 113.

Scheme II. Conversion of 1,6-Oxido[10]annulene (1) into 1-Naphthyl Hydrogen Sulfate and 1-Naphthol



tively fairly small (Table IV). The product formation may be explained by Scheme II. In view of the higher electron-demanding effect of the 1,6-oxonium sulfate bridge of **19** (X = SO_3), as compared with the 1,6-oxido bridge of **1**, the relative content of the norcaradiene type of valence isomer will be considerably greater for the equilibrium 3 than 1.[24,25] In view of the formal positive charge on the oxygen, the rate of valence tautomerization to the 1,6-oxido-1,6-dihydronaphthalene type of structure will be much greater for **20** than **18**. It is therefore proposed that the effective route for the skeletal rearrangement of **1** leading to the hydrogen sulfate **4** is 2–6.

At the very beginning the reaction system is fully aprotic and the only sequence of reactions taking place is 2–6 with X = SO_3 leading to 1-naphthyl hydrogen sulfate. This hydrogen sulfate is a strong Brønsted acid and accordingly protonation of **1** will occur [equilibrium 2, X = H^+] with formation of **19** (X = H^+) which species yields 1-naphthol by the sequence 3, 4, 7, 8.

The ring-substituted sulfonic acids **5–8** formed at temperatures >−30 °C are thought to result by sulfonation of the rearranged products **3** and **4**, since the reaction of **1** with 1 equiv of SO_3 yields to the 2- and 4-sulfonic acid in the same ratio (2.0 ± 0.2), as observed for the reaction of 1-naphthol (**3**) (1.8 ± 0.2).[18]

1-Aminonaphthalene and 1,6-Imino[10]annulene. The reactions of the two nitrogen containing substrates **2** and **10** with SO_3 in dioxane proceed heterogeneously.

The sulfonation of 1-aminonaphthalene (**10**) with 1 equiv of SO_3 at 35 °C is though to lead initially to 1-naphthylsulfamic acid **11** as the kinetic product, which by slow regeneration of **10** and SO_3 is eventually converted into the thermodynamically more stable 2- and 4-sulfonic acids of 1-aminonaphthalene. With a large excess of SO_3 relative to the amount of **10** the initially formed **11** will be sulfonated, leading to 4-sulfo-1-naphthylsulfamic acid and subsequently to 2,4-disulfo-1-naphthylsulfamic acid which (upon working up or even before) will lose SO_3 to yield the observed 1-aminonaphthalene-2,4-disulfonic acid.[12,26] As yet there is no evidence to decide whether the 1-aminonaphthalene-2-sulfonic acid is formed via a similar route as the 4-sulfonic acid or via an intramolecular rearrangement of **11**.

1,6-Imino[10]annulene upon reaction with SO_3 at 35 °C is initially completely converted into the sulfamic acid **9**. Eventually and after working up the heterogeneous reaction mixture (by which procedure the sulfamic acids of 1-aminonaphthalene **10** and the sulfonic acids of **10** will lose their *N*-sulfonic acid group[12]) 1-aminonaphthalene-4- (**13**), possibly-2- (**12**), and -2,4-disulfonic acid (**14**) are obtained. The conversion of **2** into (the sulfamic acids of) the sulfonic acids of **10** is thought to proceed via the dipolar 1,6-iminium[10]annulene-O-sulfonate species in a similar fashion as shown for the oxygen analogue **19** (X = SO_3) in Scheme I.

The presently observed acid induced skeleton rearrangements of 1,6-oxido- and 1,6-imino[10]annulene to the sulfo derivatives of 1-naphthol and 1-aminonaphthalene are related to (i) the rearrangement of the cation of 1,6-methano[10]annulene, formed by protonation at C(2) upon dissolution in FSO_3H–SO_2ClF at low temperatures, yielding the 1,2-methano-1,2-dihydro-4-naphthalenium ion[5b] and (ii) the base-catalyzed conversion of 1,6-oxido-[10]annulene to the 1-naphtholate anion upon reaction with potassium amide in liquid ammonia.[29]

Experimental Section

The [10]annulenes **1** and **2** were obtained as a gift from Prof. E. Vogel. The disulfonic acid **8** was obtained by reaction of **3** with

(24) Cremer, D.; Dick, B. *Angew Chem.* **1982**, *94*, 877; Cremer, D.; Kraka, E. *J. Am. Chem. Soc.* **1985**, *107*, 3800 (in particular 3809).

(25) Recent ab inito calculations have shown that the concentration of **19** is less than 1% of that of **20**; Cremer, D., private communication.

(26) The heterogeneous reaction of 2,6-dimethylaniline with SO_3 in nitromethane proceeds similarly as proposed in the present paper for 1-aminonaphthalene, the f_3/f_4 sulfonation ratio on using 1.0 and 8 equiv of SO_3 being ≤0.01 and 3.3, respectively. The former value is the partial rate factor ratio for the C-sulfodeprotonation of the amine proper, whereas the latter is that of the corresponding sulfamate.[27] Also the homogeneous conversion of phenylsulfamic acid in a large excess of 96–100% H_2SO_4 yields orthanalic and sulfanilic acid intermolecularly by initial C-sulfodeprotonation and subsequent N-protodesulfonation.[28]

(27) de Wit, P.; Cerfontain, H., unpublished results.

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4.0 equiv of SO_3 in nitromethane at 0 °C and its dipotassium salt isolated after the addition of excess of water, neutralization with aqueous KOH, and freeze drying. Samples of **3**, **10**, and the potassium salts of **5**, **6**, and **12** were obtained commercially from Merck and Fluka. The ^1H NMR spectra were recorded on a Bruker WM-250 spectrometer.

Sulfonation Procedures and Analysis. Procedure A. To a heterogeneous mixture of 2.0 or 5.0 equiv of SO_3 in 0.70 mL of ($^2H_8$)dioxane was added, while stirring under nitrogen, at 15 °C a solution of 0.25 mmol of the substrate in 0.70 mL of ($^2H_8$)dioxane and the temperature of the mixture subsequently adjusted. With the substrates **1**, **3**, and **15** the reaction mixtures were homogeneous, whereas with **2** and **10** they proved to be heterogeneous.

Procedure B. To a heterogeneous mixture of 0.7, 1.0, or 1.2 equiv of SO_3 in 0.20 mL of ($^2H_8$)dioxane was added at 15 °C 0.40 mL of ($^2H_2$)methylene chloride and the temperature lowered to −70 °C. To this solution was then added at −70 °C a solution of 0.25 mmol of the substrate in 0.60 mL of ($^2H_2$)methylene chloride precooled at −70 °C.

Of the homogeneous reaction mixtures, obtained by the procedures A and B, the progress of the reaction was monitored by ^1H NMR by recording spectra after appropriate time intervals. For the low-temperature experiments the temperature of the reaction mixture was raised by 10 °C a time and then kept constant for a chosen period of time. Ultimately, all the reaction mixtures were worked up by pouring them into 2–3 mL of water and adding dilute aqueous KOH till the pH was between 7.5 and 8.5. The solvents of the resulting solution were removed by freeze-drying and their NMR spectra, using ($^2H_2$)water and/or ($^2H_6$)Me_2SO as solvent, recorded.

Analysis. The components of the reaction mixtures resulting from **1** and **3** have been assigned on the basis of both the ^1H and ^{13}C NMR signals of authentic samples of **3**, **5**, **6**, and **8** in ($^2H_2$)water and ($^2H_6$)Me_2SO at the same alkalinity as the worked up reaction mixture samples. The ^{13}C NMR chemical shifts of **5**, **6**, and **8** are listed in Table III (supplementary material).

The components of the reaction mixtures of **2** and **10** were assigned (i) on the basis of a comparison of the ^1H NMR signals with those of an authentic sample of **13** by application of the sulfo and amino substituent shifts, the relative intensities, and the multiplicities of the various signals.

The presence of each of the following assigned components **3**, **5**, **6**, **8**, **10**, and **13** in the various worked up reaction mixtures was further established unequivocally by showing that addition of an equimolar amount of an authentic sample of the sulfonate in question to the soltuion to be analyzed did not lead to an enhancement of the number of ^1H NMR signals.

The procedures for the sulfonation in nitromethane and the subsequent workup and isolation of the potassium sulfonates were dscribed before.[13]

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Registry No. **1**, 4759-11-9; **2**, 4753-55-3; **3**, 90-15-3; **4**, 3197-94-2; **5**, 567-18-0; **6**, 84-87-7; **7**, 102234-08-2; **8**, 1857-16-5; **9**, 102234-09-3; **10**, 134-32-7; **11**, 24344-19-2; **12**, 81-06-1; **13**, 84-86-6; **14**, 14245-99-9; **15**, 36628-80-5; SO_3, 7446-11-9; 11-oxo-2-sulfo-1,6-methano[10]-annulene, 102234-10-6; 2,7-disulfo-11-oxo-1,6-methano[10]-annulene, 102234-11-7.

Supplementary Material Available: ^1H and ^{13}C NMR spectral data of **1–3**, **10**, and **15** and their sulfo products in various solvents [($^2H_8$)dioxane, ($^2H_8$)dioxane/($^2H_2$)methylene chloride (5:1, v/v), ($^2H_6$)Me_2SO, and ($^2H_2$)water] and a reaction scheme (6 pages). Ordering information is given on any current masthead page.

Dianions from 2,3-Dimethyl-2-butene. Metalation–Elimination in an Acyclic System

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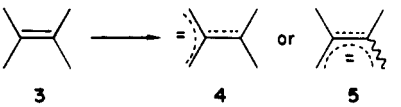
The metalation of 2,3-dimethyl-2-butene results in the preferential formation of cross-conjugated dianions which agrees with predictions from the resonance energy per atom (REPA) calculation on unsubstituted dianions. In addition, metalation with potassium *tert*-butoxide/*n*-butyllithium results in elimination to the mono- and dianions of 2,3-dimethylbutadiene, the first elimination with this metalating system reported in an acyclic system. An examination of acyclic and cyclic dianions with the potential for elimination shows that for acyclic and small (≤6) ring hydrocarbons, elimination occurs to form mono- or dianions with REPA values ≥0.060β. For seven- or eight-membered rings, REPA values are not reliable in predicting elimination.

We have been involved in an examination of factors affecting the stability of delocalized dianions.[1-3] We have determined that cross-conjugated dianions are thermodynamically more stable than linearly conjugated dianions. This enhanced stability has been attributed to Y-aromaticity.[4,5] In systems in which multiple delocalized dianions are possible, the use of REPA[6,7] values has effectively predicted the relative stabilities and therefore concentrations of the various dianionic species present.[2,3]

Scheme I



3 4 5

When 2-methyl-2-butene is dimetalated by using either *n*-butyllithium/tetramethylethylenediamine (TMEDA) or

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