Relative Intramolecular Reactivity of a π Double Bond and the 10π Annulene Moiety toward Sulfur Trioxide: Sulfonation of 11-Methylene-1,6-methano[10]annulene, 12,12-Dimethyl-11-methylene-1,6-methano[10]annulene, and 11-Oxo-1,6-methano[10]annulene with SO_3[†]

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The sulfonation of 11-methylene-1,6-methano[10]annulene (**1**), its 12,12-dimethyl derivative (**2**), and 11-oxo-1,6-methano[10]annulene (**3**) with SO_3 in dioxane and nitromethane has been studied, and the results have been compared with those of the parent 1,6-methano[10]annulene (**6**). The initial sulfonation of **1** and **3** occurs exclusively at the 2-position and that of **2** very predominantly at that position. The further ring sulfonation of the [10]annulene moiety of **1** and **2** leads to a mixture of the 2,4-, 2,7-, and 2,8-disulfonic acids of which the 2,7-isomer predominates. For 1-2-sulfonic acid in nitromethane the 12,11-sultone formation is competitive with the introduction of the second sulfo group at the [10]annulene ring, and in the presence of a sufficiently large amount of SO_3 eventually a mixture of the 2,4-, 2,7-, and 2,8-disulfonic acid of the 12,11-pyrosultones **4b** and **5b** is formed. The eventual sulfonation products of **2** by application of 8 equiv of SO_3 in nitromethane are mainly the 2,4,7- and 2,4,8-trisulfonic acids in addition to a small amount of a species tentatively assigned to be the cation **11**. The lower selectivity for the ring sulfonation of the 2-sulfonic acids of both **1** and **2**, as compared with that of **6**, is tentatively ascribed to additional initial π-complex formation between SO_3 and the vinylidene π bond and subsequent rearrangement of these complexes to the Wheland intermediates leading to sulfonation at C(4) and C(8).

Sulfonation with the dioxane–SO_3[1] and pyridine–SO_3[2] complexes is in general much more rapid with alkenes than with simple aromatic hydrocarbons.[1] Intramolecular competition in the conjugated hydrocarbon systems styrene,[3,4] 1-vinylnaphthalene,[3,4] and 9-vinylanthracene[5] leads to preferential attack of the β-carbon of the side chain with formation of the unsaturated β-sulfonic acid.[6] Intramolecular competition in the nonconjugated 9-[(*E*)-2-butenyl]anthracene also leads to sulfonation at the side chain double bond, the products being (*E*)- and (*Z*)-1-(9-anthryl)-2-butene-3-(pyro)sulfonic acid, formed in a ratio of 3:10.[5]

Sulfonation of alkenes with SO_3 yields initially a 1,2-sultone[7,8] or a 1,2-pyrosultone (also referred to as carbyl sulfate or cyclic sulfonate sulfate anhydride),[9-11] depending on the alkene to SO_3 ratio. These compounds were in a number of cases[9,10] in fact isolated, especially on starting with fluorinated alkenes.[12,13] However, upon rapidly working up the 1,2-(pyro)sultone reaction mixtures under hydrolytic conditions, in general a mixture of the corresponding β-hydroxyalkanesulfonic acid and α-alkene-γ-sulfonic acid is obtained.[3,14]

In relation to the problem of the relative reactivity of different π-electron systems and as an extension of our studies on the 1,6-methano[10]annulenes,[15-20] we have studied the sulfonation of 11-methylene-1,6-methano-[10]annulene (**1**), its 12,12-dimethyl derivative (**2**), and 11-oxo-1,6-methano[10]annulene (**3**) with SO_3. Recently the protonation of **1** with FSO_3H in SO_2ClF at −80 °C was shown to occur predominantly, if not exclusively, at C(2), illustrating the higher stability of the 11-methylene-1,6-methano[10]-2-annulenium ion as compared with the ion resulting by protonation at C(12), in agreement with semiemperical MINDO/3 and MNDO calculations.[21]

[†] Aromatic Sulfonation. 99. For part 98, see: de Wit, P.; Kruk, C.; Cerfontain, H. *Recl. Trav. Chim. Pays-Bas* **1986**, *105*, 266.

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Table III. Sulfonation of the [10]Annulenes 1–3 with SO_3 at 20 °C

no.	substr	reacn conditions: SO_3, equiv	solv[a]	t, h	unconvrtd substr, %	sulfonation products composition[b] (%): sulfonic acid products	12,11-(pyro)-sultone	12,11-(pyro)-sultone sulfonic acids
1	1	1.0	D	0.8	27	1-2-S (>98)		
2a		4.0	D	0.5	4	1-2-S (82); 1-2,4-S_2 (3); 1-2,7-S_2 (5); 1-2,8-S_2 (5)	4 (5)	
2b				5.3	<1	1-2-S (56); 1-2,4-S_2 (4); 1-2,7-S_2 (13); 1-2,8-S_2 (9)	4 (8)	4- + 5-2-S (10)
2c				29		1-2-S (45); 1-2,4-S_2 (5); 1-2,7-S_2 (17); 1-2,8-S_2 (10)	4 (9)	4- + 5-2-S (14)
3a		4.0	N[c]	1–2	<1	1-2,7-S_2 (main product)		
3b		8.0	N	1–2	<1	1-2,7-S_2 (<2)		4b-2,7-S_2 (60)
4		8.0	N[c]			1-2,4-S_2 (10); 1-2,7-S_2 (60); 1-2,8-S_2 (15); 1-2,4,7-S_3 (4); 1-2,7,12-S_3 (9)		
5	2	1.0	D	0.5	<1	2-2-S (95); 2-3-S (5)		
6a		3.0	D	24	<1	2-2-S (29); 2-2,4-S_2 (20); 2-2,7-S_2 (40); 2-2,8-S_2 (9); 2-2,4,7-S_3 (2)		
6b				168		2-2-S (3); 2-2,4-S_2 (23); 2-2,7-S_2 (55); 2-2,8-S_2 (13); 2-2,4,7-S_3 (6)		
7a		8.0	D	1.0	<1	2-2-S (78); 2-3-S (2); 2-2,4-S_2 (3); 2-2,7-S_2 (14); 2-2,8-S_2 (2)		
7b				24		2-2,4-S_2 (25); 2-2,7-S_2 (60); 2-2,8-S_2 (10); 2-2,4,7-S_3 (5)		
7c				96		2-2,4-S_2 (21); 2-2,7-S_2 (60); 2-2,8-S_2 (12); 2-2,4,7-S_3 (7)		
8a		1.6	N[d]	0.5		2-2-S (54); 2-3-S (<2); 2-2,4-S_2 (10); 2-2,7-S_2 (19); 2-2,8-S_2 (9); 2-2,4,7-S_3 (2)		
8b		1.6	N[c]	0.5		2-2-S (58); 2-3-S (<2); 2-2,4-S_2 (11); 2-2,7-S_2 (20); 2-2,8-S_2 (9); 2-2,4,7-S_3 (2)		
9a		4.0	N[c]			2-2,4-S_2 (20); 2-2,7-S_2 (43); 2-2,8-S_2 (23); 2-2,4,7-S_3 (7); 2-2,4,8-S_3 (7)		
9b		4.0	N[c]			2-2,7-S_2 (10); 2-2,4,7-S_3 (45); 2-2,4,8-S_3 (45)		
10		8.0	N[c]			2-2,7-S_2 (6); 2-2,4,7-S_3 (50); 2-2,4,8-S_3 (44)		
11	3	5.0	D[e]	3.0	13[f]	3-2-S (>98)		
				24	<1	3-2-S (>98)		
12		5.0	N[e,f]	3.0	1	3-2-S (<2); 3-2,7-S_2 (40)		

[a] D and N stand for ($^2H_8$)dioxane and ($^2H_3$)nitromethane respectively. [b] S stands for SO_3H. [c] Sulfonic acid composition calculated from the ^1H NMR spectra of the acidic reaction mixture dissolved in ^2H_2O. [d] The spectrum contains low intensity absorptions which are at lower field than those of the annulene perimeter substituted sulfonic acids [cf. Table I (supplementary material), footnote *i*]. These signals are tentatively assigned to cation **11**, which is present for ca. 3%. [e] Reaction temperature 35 °C. [f] The substrate **3** is present as its oxonium sulfonate.

Table IV. Isomer Distributions for the SO_3 Sulfonation of Some 1,6-Bridged [10]Annulenes and Their Sulfonic Acids[a]

substr	solv	T, °C	isomer distribution (%)
1	D	20	2-S (>98); 3-S (<1)
1-2-S	D	20	2,4-S_2 (11); 2,7-S_2 (37); 2,8-S_2 (23); 2-S-12,11-(pyro)sultone (29)
1-2-S[b]	N	20	2,4-S_2 (12); 2,7-S_2 (70); 2,8-S_2 (15)
2	D	20	2-S (96); 3-S (4)
	N	20	2-S (≥97); 3-S (<3)
2-2-S[b]	D	20	2,4-S_2 (29); 2,7-S_2 (61); 2,8-S_2 (10)
2-2-S	N	20	2,4-S_2 (29); 2,7-S_2 (51); 2,8-S_2 (20)
2-3-S	D	20	2,4-(≡3,5)-S_2; 2,8(≡3,7)-S_2[c]
2-2,4-S_2[c]	N	20	2,4,7-S_3 (21); 2,4,8-S_3 (79)
2-2,7-S_2[c]	N	20	2,4,7-S_3 (>98)
2-2,8-S_2[c]	N	20	2,4,8-S_3 (>98)
3	D	35	2-S (>98)
3-2-S	D	35	2,7-S_2 (40)
6	D	12, 17	2-S (>98)[15,17]
	N	0	2-S (>99)[20]
6-2-S	D	12	2,7-S_2 (>98)[17]
	N	0	2,7-S_2 (>98)[20]
6-2,7-S_2	N	20	2,4,7-S_3 (ca. 40)[27]
7	D	35	2-S (47); 7-S (53)[17]
8	D	35	2-S (>96)[17]

[a] S, D, and N stand for SO_3H, dioxane, and nitromethane, respectively. [b] Cf. footnote *c* of Table III. [c] From the composition of the reaction mixture of **2** with 8.0 equiv of SO_3 (Table III, entry 10) it follows that the rate coefficient for the conversion of the disulfonic acids is smaller for the 2,7- than the 2,4- and 2,8-isomers.

Results

The reactions of the [10]annulenes with SO_3 were studied in both ($^2H_8$)dioxane and ($^2H_3$)nitromethane as solvent. The ^1H and ^{13}C NMR assignments of the substrates and the ^1H NMR assignments of the sulfo products are compiled in Tables I and II (supplementary material). The compositions of the reaction product mixtures in the aprotic kinetically controlled[16,22] SO_3 sulfonations were determined by ^1H NMR multicomponent analysis on the basis of the specific absorption(s) of the various components[23] and are compiled in Table III.

11-Methylene-1,6-methano[10]annulene (1). The monosulfonation of **1** in dioxane leads to the formation of the 2-sulfonic acid as the only ^1H NMR detectable product, illustrating $k_2/k_3 \geq 50$. The further sulfonation of the 2-sulfonic acid leads to both substitution of the [10]-annulene ring at C(4), C(7), and C(8) with formation of the 2,4-, 2,7-, and 2,8-disulfonic acid, and to addition at the C(11)–C(12) double bond with formation of the 12,11-(pyro)sultones (**4** and/or **5**), the ratio $k_{2S\rightarrow4}/k_{2S\rightarrow7}/k_{2S\rightarrow8}/k_{2S\rightarrow sultone}$ being 11:37:23:29. The rate of sulfonation of the 2-sulfonic acid of **1** is comparable with that of the 2-sulfonic acid of the parent 1,6-methano[10]annulene **6**.[24]

The ^1H NMR spectrum of the reaction mixture of **1** with 8 equiv of SO_3 in nitromethane exhibits a predominating ABXCDY pattern for the annulenic hydrogens of the 2,7-disulfonic acid moiety and an AB system at 3.56 and 3.39 ppm (J = 4.2 Hz), which are signals assigned to the 12,11-pyrosultone of 1-2,7-disulfonic acid (i.e., **4b**-2,7-di-

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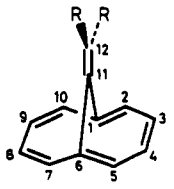
(24) In dioxane, the reaction of **6** with 3.0 equiv of SO_3 at 17 °C for 0.5 h leads to complete substrate conversion with formation of 77% 2-sulfonic acid and 23% 2,7-disulfonic acid,[17] whereas **1** with 4.0 equiv of SO_3 at 20 °C for 0.5 h leads to 96% conversion of the substrate with formation 5% 12,11-(pyro)sultone **4**, 82% 2-sulfonic acid, 3% 2,4-, 5% 2,7-, and 5% 2,8-disulfonic acid (see Table III, entry 2a).



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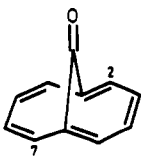
2 $R^1 = R^2 = Me$



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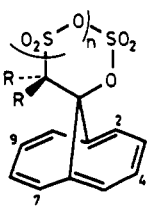

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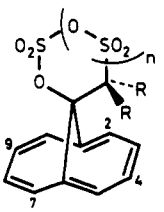
9a R = Me ; n = 0
9b R = Me ; n = 1



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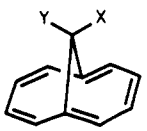
5b R = H ; n = 1
10a R = Me ; n = 0
10b R = Me ; n = 1



6 X = Y = H
7 X = F ; Y = H
8 X = Y = F

sulfonic acid). Upon addition of ^2H_2O both the doubling of the NMR pattern of the annulenic hydrogens and the AB pattern of the pyrosultone methylene group have disappeared and the NMR pattern is again that of a mixture of mainly the 2,4-, 2,7-, and 2,8-disulfonic acids of **1**, the amount of trisulfonic acids being only 13%.

12,12-Dimethyl-11-methylene-1,6-methano[10]annulene (2). The monosulfonation of **2** in dioxane leads to the formation of the 2- and 3-sulfonic acid in a ratio of 96:4. The further sulfonation of the 3-sulfonic acid will lead to substitution of the 5- and 7-positions rather than the 10-position as result of the directing effect of the sulfonic acid substituent at C(3)[25] with formation of the 2,4(≡3,5)- and 2,8(≡3,7)-disulfonic acids. The further sulfonation of the 2-sulfonic acid results in the formation of the 2,4-, 2,7-, and 2,8-disulfonic acids, the ratio of $k_{2S\rightarrow4}/k_{2S\rightarrow7}/k_{2S\rightarrow8}$ being 29:61:10. As appears from a comparison of the product compositions of the reactions in dioxane of **1** with 4.0 equiv of SO_3 for 29 h and of **2** with 3.0 equiv of SO_3 for 24 h (cf. Table III, entries 2c and 6a), the rate of sulfonation is a factor of ca. 2 greater for 2-2-SO_3H than 1-2-SO_3H.

The reaction of **2** with SO_3 in nitromethane is rapid. With 1.6 equiv of SO_3 and a reaction time of 0.5 h, the substrate is converted completely, and the resulting 2-sulfonic acid is again converted for ca. 40%. With 4.0 equiv of SO_3 the ^1H NMR spectra of the reaction mixtures in ($^2H_3$)nitromethane contain in addition to the aromatic and methyl signals of the 2,4-di, 2,7-di, 2,8-di-, 2,4,7-tri-, and 2,4,8-trisulfonic acids [as—with the exception of the latter component—were observed on using 1.6 equiv of SO_3 (cf. Table III, entry 8a)] aromatic signals in between 8.9 and 10.2 ppm and a methyl signal at 2.34 ppm, i.e., all at lower field than those of the ring-substituted sulfonic acids of **2**. The same low-field absorptions were observed for reaction mixtures using 8.0 equiv of SO_3. The very low field absorptions in ($^2H_3$)nitromethane exclude the possibility of the presence of sulfonic acids of the 12,11-(pyro)sultones **9** and **10**, since the sulfonic acids of the homologous 12,11-(pyro)sultones **4** and **5** in nitromethane do not exhibit ^1H NMR signals at >9.2 ppm. The very low field absorptions were tentatively assigned to the cation **11**.[26] With 4 and 8 equiv of SO_3 the yields of **11** are ca. 7% and 28%, respectively.

The further ring sulfonation of the initially formed 2-2-sulfonic acid results in the formation of the 2,4-, 2,7-, and 2,8-disulfonic acids, the ratio of $k_{2S\rightarrow4}/k_{2S\rightarrow7}/k_{2S\rightarrow8}$ being 29:51:20. Upon sulfonation of **2** in nitromethane with a sufficiently large amount of SO_3 and subsequent reaction with water the resulting aqueous trisulfonic acid mixture will contain 56% of the 2,4,7-isomer and 44% of the 2,4,8-isomer (cf. Table III, entry 10). The routes by which these ring substituted trisulfonic acids are formed and their relative importance are shown in Figure 1.

11-Oxo-1,6-methano[10]annulene (3). The sulfonation of **3** with 5.0 equiv of SO_3 in dioxane at 35 °C leads to the formation of the 2-sulfonic acid as the only product. The unconverted substrate is (predominantly) present in the form of the oxonium sulfonate **12**. This was concluded from the lower field absorption of the two ^1H NMR AA'BB' multiplets observed for the reaction mixture of **3** with SO_3 as compared with those of **3** proper in the same solvent, the two multiplets being centered at 7.76 and 7.54 vs. 7.60 and 7.42 ppm, respectively. The rate of formation of the 2-sulfonic acid is substantially smaller for **3** than **1** (cf. Table III, entries 2 and 11). The sulfonation of **3** with 5.0 equiv of SO_3 in nitromethane at 35 °C for 3 h yields 40% 2,7-disulfonic acid in addition to other (as yet unassigned) products.

Sulfonation Isomer Distributions. The sulfonation isomer distributions of the [10]annulenes **1–3** and their mono- and disulfonic acids, as estimated from the various observed compositions of the reaction mixtures (see Experimental Section), are compiled in Table IV, together with those of some related [10]annulenes.

Discussion

The initial sulfonation of the hydrocarbons **1** and **2** takes place at C(2) of the annulene moiety and not at one of the carbons of the vinylidene bridge, just as was observed for the protonation of **2**, which occurs selectively at C(2).[21] The preferential electrophilic attack at C(2) of the annulene moiety is in agreement with semiemperical calculations which showed **13** to be more stable than **14**, the energy differences being 57.3 (MINDO/3) and 118.8 kJ/

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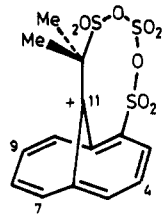
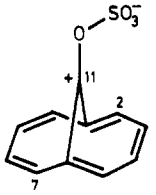
(26) After the addition of ^2H_2O to the reaction mixtures all the products with the exception of (the product derived from) the cation **11** were found in the aqueous solution.

(27) Reaction of **6** (0.23 mmol) dissolved in ($^2H_3$)nitromethane (0.5 mL) with 8.0 equiv of SO_3 (76 μL) at 20 °C showed by ^1H NMR after 20 min the presence of ca. 40% of 6-2,4,7-trisulfonic acid in addition to carbon skeleton rearranged products. No further change of the ^1H NMR occurred over a period of a day: ^1H NMR δ 9.21 [s, H(5)], 8.74 [s, H(3)], 8.67 [d, J = 9.5 Hz, H(10)], 8.35 [d, J = 9.7 Hz, H(8)], 7.92 [t, J = 9.6 Hz, H(9)], −0.02 + −0.38 [AB, J = 10 Hz, C(11)H_2]. ^1H NMR of the isolated tripotassium trisulfonate dissolved in ^2H_2O: δ 8.83 [s, H(5)], 8.40 [s, H(3)], 8.24 [d, J = 9.2 Hz, H(10)], 7.94 [d, J = 9.6 Hz, H(8)], 7.47 [t, J = 9.4 Hz, H(9)], −0.10 + −0.27 [AB, J = 10 Hz, C(11)H_2].[28]

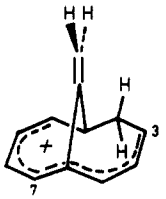
(28) de Wit, P.; Cerfontain, H., unpublished results.



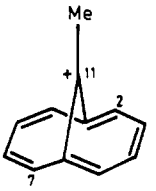
11



12



13



14

mol (MNDO).[21] The frontier orbital approach also seems to favor the formation of **13**.[21,29]

The sulfonation of **1**-2-sulfonic acid with ≥4.0 equiv of SO_3 in both dioxane and nitromethane leads to sulfodeprotonation at the 4-, 7-, and 8-positions and to 12,11-(pyro)sultone formation as competing processes; in nitromethane with 8.0 equiv of SO_3 subsequently the 12,11-pyrosultone of **1**-2,7-disulfonic acid is observed as additional component. Upon addition of water a mixture of mainly **1**-2,7-disulfonic acid and small amounts of the 2,4-di-, 2,8-di-, 2,4,7-tri-, and 2,4,8-trisulfonic acid of **1** is formed.

Sulfonation of **2**-2-sulfonic acid in both dioxane and nitromethane leads predominantly to sulfodeprotonation at the [10]annulene ring positions 4, 7 and 8. In nitromethane with 8.0 equiv of SO_3 and subsequent treatment with water, the aqueous solution contains a mixture of mainly the 2,4,7- and 2,4,8-trisulfonic acids of **2**.

The rates of sulfonation of the 2-sulfonic acids decrease in the order **2** > **1** ≃ **6** ≫ **3**.[34] The comparable reactivity of **1**-2-SO_3H and **6**-2-SO_3H is in agreement with the very comparable calculated proton affinities of **1** and **6** at C(2).[21] The higher reactivity of **2**-2-SO_3H as compared with **1**-2-SO_3H may be explained in terms of the higher through-bond inductive effect of the dimethylvinylidene as compared with the vinylidene bridge due to the additional methyls.[32] The relatively very low reactivity of 11-oxo-1,6-methano[10]annulene **3** for electrophilic SO_3 sulfonation is due in part to the substrate proper which carries a partial positive charge on C(11). However it is mainly ascribed to the O-sulfonation of **3** with formation of **12**, which further enhances the positive charge at C(11) and thus leads to an enhanced destabilization of the σ complex for 2-sulfonation.

The selectivity in the monosulfonation of **2** in dioxane is only somewhat lower than that of 1,6-methano[10]-annulene (**6**), but the selectivities of **1**-2-SO_3H and **2**-2-SO_3H are both very substantially lower than that of **6**-2-SO_3H (cf. Table IV) in that there is β-substitution at C(4) and C(8) in addition to substitution at C(7). This is probably due to the additional vinylidene bridge and may be explained in terms of π-complex formation between SO_3 and the vinylidene π bond of the 2-sulfonic acids of **1** and **2**, which then have to rearrange—at least in part—to the σ complexes for β-substitution at C(4) and C(8).

Sulfonation Isomer Distributions. The sulfonation of **1**, just like that of **6**,[15,17,20] **7**,[17] and **8**[17] proceeds highly selectivity at the 2-position, illustrating a very much higher reactivity of the α- than the β-positions. The sulfonation of **2** is somewhat less selective, but the degree of 2-substitution is still ≥96%.

The sulfonic acid isomer distributions for the further sulfonation of the sulfonic acids of **1** and **2** clearly demonstrate that the sulfonic acid groups already present in the substrate undergoing substitution are important in governing the positional reactivity order.[35] Upon monosulfonation of **1**–**3** the α-positions are by far the most reactive ones. Upon sulfonation of the 2-sulfonic acid of both **1** and **2**, seven disulfonic acids are a priori expected to be formed. The 2,3- and 2,10-disulfonic acids are not formed, since sulfonation ortho or peri to a sulfo group is prevented by steric hindrance.[35,36] The absence of any 2,5-disulfonic acid is ascribed to the stronger deactivating effect of the 2-sulfo group upon forming the σ-complex for sulfonation at the neighboring C(5) than at the more remote C(7)–C(10) moiety. On the basis of the substituent effect of the sulfonic acid group at C(2), one would expect the isomer ratio for β-substitution to follow the order 2,4- ≃ 2,8- ≫ 2,9-disulfonic acid, since the formation of the latter—in contrast to the former two disulfonic acids—is deactivated electronically by the 2-sulfo group. The observed partial rate factor ratios for the sulfonation of the [10]annulene moiety of **1**-2-SO_3H in dioxane and nitromethane are in fact $f_4/f_7/f_8/f_9$ = 15:51:32:≤2 and 12:71:15:≤2, respectively, and those for the sulfonation of **2**-2-SO_3H in dioxane and nitromethane are 29:60:10:≤2 and 29:50:20:≤2, respectively. The substitution of the 2-sulfonic acid at C(7) is also deactivated by the 2-sulfo group. The predominant formation of the 2,7-isomer then illustrates that the directing effect of the parent hydrocarbon overrules the deactivating effect of the sulfo substituent in the substrate.

As to the substitution of **2**-2,4-disulfonic acid at C(7), C(8), and C(9), the first one is a (favored!) α-substitution

(29) The high reactivity of [10]annulenes toward SO_3 sulfonation[30] may infer that the transition state for the formation of the intermediate (σ) complexes will very much resemble the reactants[31] rendering the frontier orbital approach applicable. As appears from photoelectron studies[32] the bridge olefin MO of both **1** and **2** are only the fourth and third highest occupied levels, respectively. Assuming the most probable attack to take place by interaction between the LUMO of SO_3[33] and that MO of the vinylidene[10]annulene with which maximal mixing is possible (provided that no symmetry-imposed impediments act apart), then it is clear that the bridge olefin MO will be a poor choice, the amount of effective mixing of the two MO's being proportional to the inverse of their energy difference. Consistent with the observed energy order of the MO orbitals, the initial sulfonation takes in fact place at the [10]annulene ring.

(30) The reactivity of **6** for sulfonation by SO_3 in dioxane is at least 3×10^7 times that of naphthalene.[17]

(31) Hammond, G. S. *J. Am. Chem. Soc.* **1955**, *77*, 334.

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(34) In the preliminary communication it was concluded erroneously from the 100-MHz ^1H NMR spectra that **1** with ≥3 equiv of SO_3 in dioxane does not undergo disulfonation.[16]

(35) The positional reactivity order for the sulfodeprotonation of sulfonic acids of aromatic hydrocarbons is governed by three factors, viz., (i) the differences in the cation localization energies (L's) of the positions under scrutiny of the parent hydrocarbon, (ii) the differences in steric hindrances for the introduction of the sulfo groups at these positions, and (iii) the electronic directing effect of the sulfonic substituent(s) already present in the substrate in destabilizing the σ complexes under comparison.[25]

(36) In the naphthalene and [10]annulene series, compounds with two sulfo groups in peri orientation have to the best of our knowledge not been described.

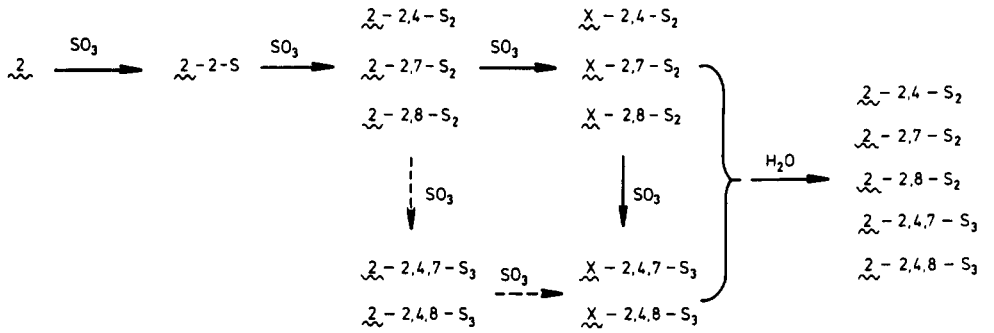


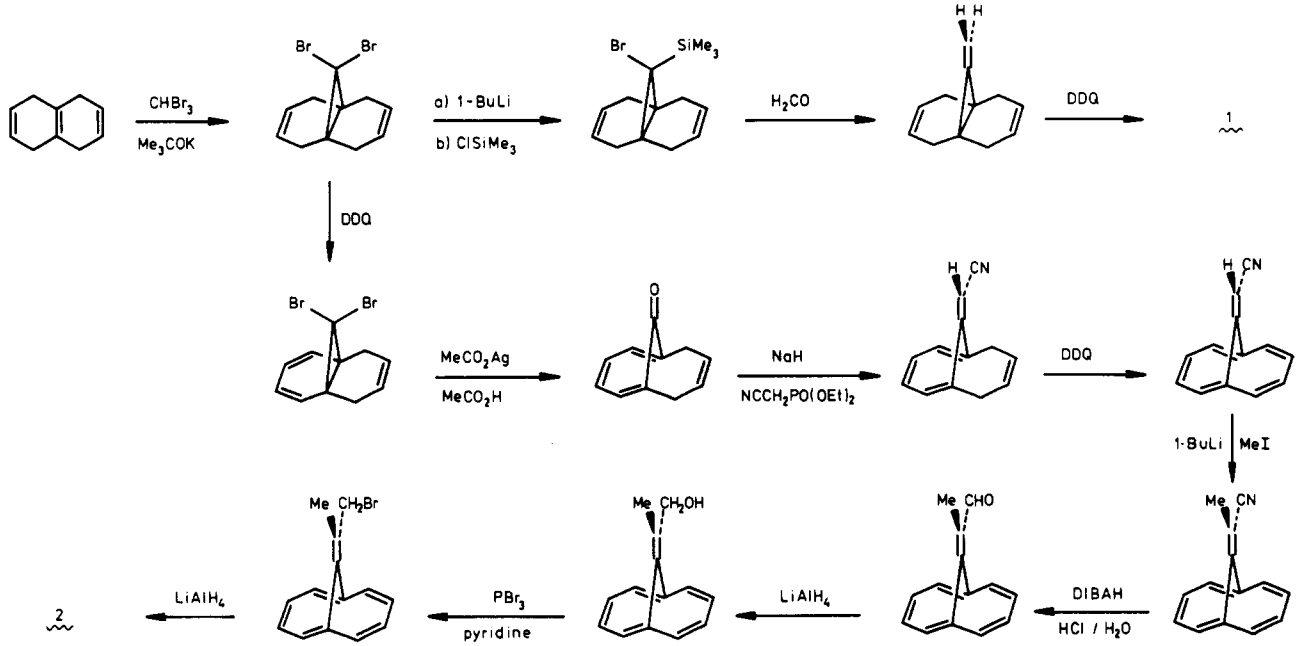
Figure 1. Sulfonic acid isomer distributions and isomeric sulfonation ratios for the reaction of **2** with SO_3 in nitromethane after aqueous workup.[26]

Table V. Observed and Predicted Ring Positional Reactivity Orders of the [10]Annulenes 1 and 2 (ArH) and Their Sulfonic Acids

	reactivity order				
	predicted on the basis of			observed	
sulfo subst[a]	steric hindrance[b]	ΔL(ArH)	electronic subst eff S[a]	1	2
		$2 \gg 3$[21]		$2 \gg 3$	$2 \gg 3$
2-S	$10 < 3 \ll$ others	$5 = 7 = 10 \gg$ others	$4 = 8 = 10 \gg$ others	$7 > 8 > 4$	$7 > 4 > 8$
3-S	$2 = 4 \ll$ others	$2 = 5 = 7 = 10 \gg$ others	$5 = 7 = 9 \gg$ others		
2,4-S_2	$10 < 3 < 5 \ll$ others	$5 = 7 = 10 \gg$ others	$8 = 10 \gg$ others		$8 > 7$
2,7-S_2	$5 = 10 < 3 = 8 \ll 4 = 9$	$5 = 10 \gg$ others	$3 = 4 = 5 = 8 = 9 = 10$		4
2,8-S_2	$10 < 3 = 7 \ll$ others	$5 = 7 = 10 \gg$ others	$4 = 10 \gg$ others		4

[a] S stands for SO_3H. [b] The steric hindrance for substitution is considered to increase in the order: ortho to a sulfo group < ortho in between two sulfo groups in meta orientation < peri to a sulfo group (ref 35).

Scheme I. Synthesis of 1 and 2 Starting from 1,4,5,8-Tetrahydronaphthalene[a]



[a] DDQ and DIBAH stand for 2,3-dichloro-5,6-dicyano-1,4-benzoquinone and diisobutylaluminum hydride, respectively.

but deactivated by the two sulfo groups, the second one is at a β-position but not directly deactivated by any of the two sulfo groups, and the third one at C(9) is at a β-position and further deactivated by the two sulfo groups. In fact, the latter substitution does not occur and the observed f_7/f_8 ratio of 0.27 indicates that the preference of α- over β-substitution is overruled by the deactivation by two sulfo groups: thus electronic directing effect of one sulfo substituent < α- over β-preference < electronic directing effect of two sulfo substituents. With 2-2,7-disulfonic acid the sulfonations at C(3) and C(5) are sterically prevented, leaving the sulfonation to occur at C(4) which is a β-position and deactivated by the 7-sulfo group.[37] As to the sulfonation of 2-2,8-disulfonic acid at C(4) and C(5) the former is a β-substitution not directly deactivated by the sulfo substituents and the latter an α-substitution but deactivated by both the 2- and 8-sulfo groups. The 2-2,5,8-trisulfonic acid is not observed as a product, again indicating that the preference for α- over β-substitution

(37) With **6** in nitromethane the only disulfonic acid formed is the 2,7-isomer.[20] Its further sulfonation with an excess of SO_3 in fact only yields the 2,4,7-trisulfonic acid (ca. 40%) in addition to carbon skeleton rearranged products.[27]

is overruled by the deactivation of two sulfo substituents.

A compilation of the observed and predicted[35] positional reactivity orders for the [10]annulenes **1** and **2** is given in Table V. On the basis of additivity of the effects of the [10]annulene group and the sulfo groups (see before) and the data of Table IV it follows that $k_{2,8\rightarrow4} = k_{2,4\rightarrow8} > k_{2,4\rightarrow7} > k_{2,7\rightarrow4}$. Accordingly the rate of conversion of the disulfonic acids will decrease in the order 2,4- > 2,8- > 2,7-disulfonic acid. The lower reactivity of the 2,7-isomer is actually apparent in the **2** series (cf. Table III, entries 9a,b and 10).

Experimental Section

Starting from 1,4,5,8-tetrahydronaphthalene,[38] the [10]-annulenes **1** and **2** were synthesized, following the sequences shown in Scheme I, as described extensively elsewhere.[39,40] The synthesis of **3** was reported before.[41]

The sulfonation in dioxane as solvent was effected by adding at ca. 20 °C 0.4 mmol of the [10]annulene in ($^2H_8$)dioxane (0.30 mL) to the (heterogeneous) solution of the desired amount of SO_3 in ($^2H_8$)dioxane (1.00 mL). The sulfonation in nitromethane was effected by adding to 0.4 mmol of the [10]annulene in ($^2H_3$)-nitromethane (0.40 mL) at ca. 20 °C a solution of the desired amount of SO_3 in ($^2H_3$)nitromethane (1.00 mL). The progress of the reaction was determined by recording ^1H NMR spectra at appropriate time intervals. In a number of cases, the reaction mixtures were quenched with ^2H_2O, the aprotic solvents removed by separation or—after neutralization—by freeze-drying and subsequent dissolution of the residual salts in ^2H_2O, and the ^1H NMR spectra of the resulting solutions of the sulfonic acids or sulfonates in ^2H_2O recorded. The ^1H NMR spectra were recorded with a Varian XL-12 CW and a Bruker WM-250 spectrometer with reference to $SiMe_4$ as virtual internal standard.

The sulfo product compositions of the various reaction mixtures were determined by multicomponent ^1H NMR analysis.[23] For the various mono- and disulfonic acids, the sulfonation isomer distribution ratios have been calculated from the compositions of the mono- and disulfonic acids and the di- and trisulfonic acid mixtures, respectively, by the method exemplified before for 1,2,3-trimethylnaphthalene-5-sulfonic acid,[42] assuming the very small amounts of the 2,4,7-trisulfonic acids of **2** present in the reaction mixture (cf. Table III, entry 8a) to result for 50% from the corresponding 2,4- and 2,7-disulfonic acids.

Acknowledgment. We thank Drs. S.M. van der Kerk and P. de Wit for valuable discussions and Mr. C. Kruk and Mmes N.E. Bruinzeel, H. van der Laan-Ctvrteckova, and C. A. M. Mittendorf-van Rijn for recording the NMR spectra.

Registry No. 1, 10474-24-5; 1-2-S, 79865-00-2; 1-2,4-S_2, 108743-77-7; 1-2,7-S_2, 108743-78-8; 1-2,8-S_2, 108743-79-9; 1-2,4,7-S_3, 108743-80-2; 1-2,7,12-S_3, 108743-81-3; **2**, 88635-77-2; **2**-2-S, 108743-82-4; **2**-3-S, 108743-83-5; **2**-2,4-S_2, 108743-84-6; **2**-2,7-S_2, 108743-85-7; **2**-2,8-S_2, 108743-86-8; **2**-2,4,7-S_3, 108743-87-9; **2**-2,4,8-S_3, 108743-88-0; **3**, 36628-80-5; **3**-2-S, 102234-10-6; **3**-2,7-S_2, 108743-89-1; **4a**, 108772-64-1; **4b**-2,7-S_2, 108743-90-4; **5a**-2-S, 108743-91-5.

Supplementary Material Available: ^1H and ^{13}C NMR spectral data of 1–3 and their sulfonation products in ($^2H_8$)dioxane, ($^2H_3$)nitromethane, and ^2H_2O as solvents (4 pages). Ordering information is given on any current masthead page. Syntheses of 1 and 2 starting from 1,4,5,8-tetrahydronaphthalene are given in ref 39.

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Retro-Ene Reactions of N-Substituted Derivatives of 4-Aza-2,2-dimethyl-1-phenyl-3-butenone and Related Compounds

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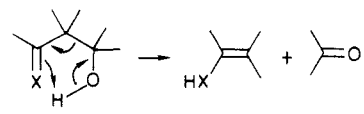
The retro-ene reactions of N-substituted derivatives of 4-aza-2,2-dimethyl-1-phenyl-3-butenone with methanol and benzylamine are described. The reactions with methanol yield methyl benzoate and N-substituted derivatives of 2-methylpropanimine. Reaction of *N*-benzyl-4-aza-2,2-dimethyl-1-phenyl-3-butenone with benzylamine yields *N*-benzyl-2-methyl-1-phenylpropanimine and *N,N'*-dibenzylformamidine.

Fragmentation reactions of the retro-ene type have been the subject of extensive studies and have been reviewed in recent times.[1,2] Many β,γ-unsaturated alcohols[3] and a few β,γ-unsaturated amines[4] undergo retro-ene fragmentations at high temperature according to the path shown in Scheme I. The thermal amine-catalyzed retro-aldol condensation also fits into this reaction system.[5] However, as a general rule, there are only a few examples where a CN double bond is utilized as the terminus for the hydrogen transfer,[6,7] and in most systems where the C=N is used it is part of a heteroaromatic system.

In a previous paper we reported the first example of retro-ene type fragmentation in acyclic iminoketones.[8]

Scheme I



Later, De Kimpe et al.[9] described a similar reaction in the fragmentation of α,α'-dichloro-β-iminocarbonyl com-

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