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Aromatic Sulfonation. 67.[1] Sulfonation of the 1,6-Methano[10]annulene System. Evidence for Ipso Attack with the 2,7-Dimethyl Derivative

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Abstract: Sulfonation of 1,6-methano[10]annulene (**1**) with 0.9 equiv of SO_3 in dioxane yields exclusively the 2-sulfonic acid, and with 4 equiv of SO_3 only the 2,7-disulfonic acid. The primary kinetic isotope effect for the monosulfonation of **1** was determined to be $k_H/k_D = 3.8 \pm 0.3$. Sulfonation of 2-methyl-**1** yielded the 5-sulfonic acid. The reaction of 2,7-dimethyl-**1** with SO_3 in dioxane resulted in peri (65%) and ipso (35%) substitution, with formation of 2,7-dimethyl-**1**-5-sulfonic acid and 2-methyl-**1**-7-sulfonic acid, respectively.

Aromaticity is an intriguing phenomenon in organic chemistry. Since the formulation of Hückel's rule there has been a dramatic search for compounds exhibiting aromaticity. Recently the monocyclic compounds containing $(4n + 2)\pi$ electrons have attracted much attention. In 1964 Vogel synthesized 1,6-methano[10]annulene (**1**), a stable 10π-electron system,[2] which was subjected to various criteria developed to test for aromaticity.[3] The electrophilic aromatic reactivity of **1** was also investigated.[4] In the course of our study on bicyclic 10π-electron systems we thought it of interest to study the sulfonation of the 1,6-methano[10]annulene system.

Results and Discussion

The sulfonation reactions of the investigated compounds are presented in Scheme I. The ^1H NMR characteristics of the isolated potassium sulfonates are listed in Table I. Reaction of **1** with 0.9 equiv of SO_3 in dioxane resulted in the exclusive formation of 1,6-methano[10]annulene-2-sulfonic acid (**2**).

In order to test whether the α-substitution encounters steric hindrance from the peri hydrogen and possibly also from the methylene bridge the primary kinetic isotope effect was determined.[5] From the ratio of the mono- and dideuteriomonosulfonic acids obtained upon sulfonation of **1**-*2,7-d*$_2$ with 0.9 equiv of SO_3 in dioxane, the k_H/k_D was calculated to be 3.8 $\pm$ 0.3. The k_H/k_D for the α-sulfonation of naphthalene-*1,4-d*$_2$ with SO_3 was found to be smaller, viz., 1.9 $\pm$ 0.2 for nitromethane and 2.0 $\pm$ 0.2 for trichlorofluoromethane as solvent.[6] The larger kinetic isotope effect of **1** indicates a relative retardation of the proton removal from the σ complex.[7] This may be rationalized in terms of SO_3 attack from the bottom side of the molecule (trans to C_{11}), as the subsequent proton abstraction from C_2 of the resulting σ complex will be sterically hindered by the adjacent methylene bridge.[10]

The sulfonation of **1** is highly specific in contrast to that of naphthalene where the α:β ratio for monosubstitution with SO_3 in nitromethane at 0 °C was found to be 7.3. The high specificity for the sulfonation of **1** is in agreement with the very high partial rate factor reported for the protiodetritiation at the 2 position.[4d] For the 3 position this datum is, however, unknown. 11,11-Difluoro-1,6-methano[10]annulene,[11] which is geometrically comparable with **1**, has an α:β partial rate factor ratio for protiodetritiation of 23.3,[4d] compared with a value of 7.7 for naphthalene.[12] For the protiodetritiation the steric hindrance is thought to be "small or nonexisting" [13] in contrast to sulfonation. Thus, in spite of the absence of properly determined partial rate factors of **1**, the α:β reactivity ratio of **1** appears to be much higher than that of naphthalene and this indicates a much higher selectivity of **1** toward electrophilic substitution. The difference in α:β reactivity between **1** and naphthalene is apparently large enough to overcome the enhanced steric repulsion for α-sulfonation of **1**, as compared with naphthalene, which is apparent from the higher kinetic isotope effect of hydrogen (see before).

It is of interest to note that the isomer ratio for 9- and 1-sulfonation of anthracene is still 2.5,[14] despite the maximum kinetic isotope effect for the 9 substitution.[9] The very high reactivity of the 9 position is indicated by the high 9:1 partial rate factor ratio for protiodetritiation,[12b] which is 7.9×10^4. In this context it should be pointed out that the (stated) electrophilic bromination and nitration of **1** have been explained in terms of initial formation of addition compounds followed by elimination.[4a,15] This is of special interest for the nitration at the 3 position of **1**.[4a]

Upon reaction of **1** with 4 equiv of SO_3 in dioxane the 2,7-disulfonic acid (**3**) was formed in a yield of more than 90%. Compound **1** is the first aromatic hydrocarbon to undergo disulfonation with SO_3 in dioxane, which is a relatively mild sulfonating reagent,[16] indicating the high reactivity of **1**. Reaction of 2-methyl-1,6-methano[10]annulene (**4**) with both 0.9 and 4 equiv of SO_3 in dioxane resulted in the exclusive formation of the 5-sulfonic acid (**5**). In contrast the bromination of **4** yields not only the 5- but also the 7-monobromo compound.[4b] As no disulfonation could be accomplished this again confirms the very high α:β reactivity ratio. The high

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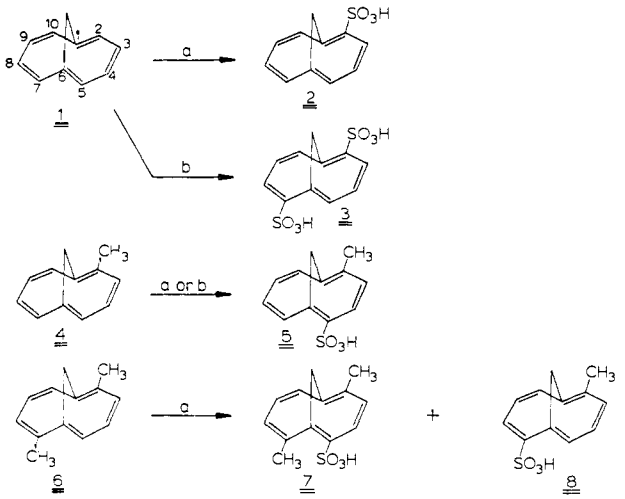
Table I. ^{1}H NMR Chemical Shifts of 1,6-Methano[10]annulene Sulfonate(s) and Some of the Methyl Derivatives in D_2O

compd	^{1}H NMR, ppm[a]								
	H_3	H_4	H_5	H_7	H_8	H_9	H_{10}	CH_2	CH_3
2	8.15 (d) J = 9	7.48 (t) J = 9	7.95 (d) J = 9	7.82 (d) J = 8	7.6[b]	7.6[b]	8.48 (d) J = 8	−0.17[c] (s)	
3	8.42 (d) J = 9.5	7.93 (t) J = 9.5	8.74 (d) J = 9		8.42 (d) J = 9.5	7.93 (t) J = 9.5	8.74 (d) J = 9	+0.10 (s)	
5	7.46 (d) J = 9.5	8.08 (d) J = 9.5		8.37 (d) J = 7	7.8[b] (m)	7.8[b] (m)	8.08 (d) J = 9	+0.18 (d, t), −0.15 (d) J = 9.5; 1.5	3.02
7	7.21 (d) J = 9.5	8.27 (d) J = 9.5			7.6[b] (m)	7.6[b] (m)	7.6[b] (m)	−0.01 (d) −0.39 (d) J = 10	2.75 (2)[d] 3.14 (7)[d]
8	7.25 (d)	7.6[b] (m)	8.42 (d)		8.08 (d)	7.6[b] (m)	7.6[b] (m)	−0.10 (d) −0.34 (d) J = 10	2.80

[a] Proton chemical shifts are referred to external Me_4Si. [b] Center of the overlapping unresolved multiplet. [c] In Me_2SO the methylene signal is an AB system (δ −0.15 and −0.28 ppm, with J = 9.5 Hz) with the lower field signals broadened. [d] The number in parentheses indicates the ring position of the methyl substituent.

Scheme I. Sulfonation of **1**, **4**, and 6 with (a) 0.9 and (b) 4 Equiv of SO_3 in Dioxane at 12 °C



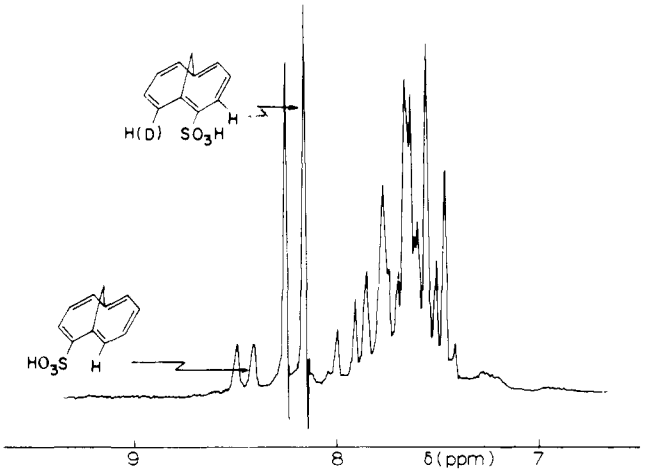


Figure 1. ^{1}H NMR spectrum of the potassium sulfonates resulting from the sulfonation of **1**-2,7-d_2 with SO_3–dioxane at 12 °C.

selectivity of the sulfonating reagent employed is confirmed by comparison of the electrophilic substitutions in 1-methylnaphthalene.[17]

In order to possibly effect β-substitution in the annulene skeleton, we studied the sulfonation of 2,7-dimethyl-1,6-methano[10]annulene (**6**), for which two of the α positions are blocked by methyl substituents and the two remaining α positions are peri to these methyl groups which were thus[18] considered sterically very inaccessible for sulfonation. Reaction of **3** with 0.9 equiv of SO_3 in dioxane resulted unexpectedly in the formation of 65 ± 5% 2,7-dimethyl-1,6-methano[10]-annulene-5-sulfonic acid (**7**) and 35 ± 5% 2-methyl-1,6-methano[10]annulene-7-sulfonic acid (**8**). The strong steric repulsion between the CH_3 and SO_3^- group of **7** is evident from its spontaneous slow desulfonation in water with re-formation of **1**. Product **8** must result from sulfodemethylation, i.e., ipso attack of SO_3 followed by demethylation. For comparison, the sulfonation of 1,5-dimethylnaphthalene (1,5-DMN) with SO_3 in nitromethane resulted exclusively in the formation of the two possible mono-β-sulfonic acids in equal amounts.[6] Protonation of 1,5-DMN showed the unsubstituted α position to be the most reactive one,[19,20] as predicted by simple Hückel MO calculations.[6] From similar type of calculations for sulfonation, i.e., with inclusion of steric parameters, it was concluded that the β-sulfonic acids result from direct substitution.[6] Further it was shown by these calculations that of all the DMNs only the sulfonation of 1,4-DMN probably in part proceeds by ipso attack of SO_3, followed by a subsequent 1,2-sulfo shift and eventual formation of the 2-sulfonic acid.[6,21]

INDO calculations[22] showed the energy differences of the σ complexes formed by protonation of **6** at the indicated position to be $\Delta E(C_2\text{-}C_3)$ = 1.48 eV; $\Delta E(C_5\text{-}C_4)$ = 0.59 eV; $\Delta E(C_3\text{-}C_4)$ = 0 eV. Accordingly the ipso position is by far the most reactive one for electrophilic attack. Apparently the energy difference between SO_3 attack at C_2 and C_3 of **6** is too large to allow a 1,2-sulfo shift. The rare demethylation pathway is apparently favored; it is thought to proceed by intramolecular attack of the pyrosulfonate group[23] at the ipso methyl yielding via a six-membered transition state the methylannulene pyrosulfonate ester. The second best place for SO_3 attack of **6** is the 5 position. From the results it is obvious that proton abstraction from the resulting σ complex yielding the sterically hindered **7** is energetically favored over the 1,2-sulfo shift, the activation energy of which is >0.59 eV. It thus appears that the β-sulfonations of **6** are overruled by the two α-substitutions, although they both have a subsequent high-energy step on the reaction pathways leading to **7** and **8**.

The ^{1}H NMR assignment of **7** and **8** is unequivocally supported by laser desorption mass spectrometry.[24] With this technique two signals were observed at *m/e* 327 and 313: the cationized molecules $[M + K]^+$ of **7** and **8**, respectively. Using field desorption[25] similar results are to be expected, and in fact the salt of **5** yielded a $[M + K]^+$ signal at *m/e* 313. However, the mass spectrum of the mixture of the potassium salts of **7**

and **8** showed three major peaks at *m/e* 324, 338, and 352 in a ratio of 1:10:2. The absence of *m/e* 313 and 327 demonstrates the instability of **7**, which apparently decomposes on the emitter, giving fragmentation and recombination of the subsequent radicals formed. Loss of the sulfonate group from **7** is thought to give a hydrocarbon radical which can dimerize to yield $C_{26}H_{26}$, or react with **8** with formation of $C_{25}H_{24}$; these hydrocarbons upon ionization then gave *m/e* 338 and 324, respectively. Mass 352 may be $C_{13}H_{13}S_2O_5K$, which could have been formed from **7** and SO_2, produced in the system.

Experimental Section

General. The ^1H NMR spectra were recorded on a Varian HA-100 and XL-100 spectrometer. Chemical shifts are reported in δ values relative to external neat tetramethylsilane (capillary). The elemental analysis was performed by Mr. H. Pieters of our microanalytical department. Electron impact mass spectra were recorded on a AEI MS 902 and the field desorption spectra on a Varian MAT 711 mass spectrometer. The laser desorption spectra were recorded on a home-built mass spectrometer equipped with simultaneous ion detection system at the FOM-Institute for Atomic and Molecular Physics, Amsterdam.

Materials. 1,6-Methano[10]annulene (**1**)[2] and its 2-methyl (**4**)[4b] and 2,7-dibromo derivatives[4b] were synthesized by known procedures. The synthesis of 2,7-dimethyl-1,6-methano[10]annulene (**6**) was performed in 90% yield according to the procedure described for **4**:[4b] ^1H NMR ($CDCl_3$) δ 7.88 (m, 2 H), 7.49 (m, 4 H), 3.02 (s, 6 H), −0.04 (s, 2 H). Anal. Calcd for $C_{13}H_{14}$: C, 91.71; H, 8.29. Found: C, 91.94; H, 8.27. 1,6-Methano[10]annulene-*2,7-d_2* was synthesized from the 2,7-dibromo precursor in the usual way.[26] The label content was determined by field desorption mass spectrometry to be 90.2% d_2, 8.9% d_1, and 0.9% d_0.

Sulfonation Procedure. Addition of SO_3 (1.8 or 8 mmol) to dioxane (~3 mL) at 12 °C resulted in a white precipitate. To the heterogeneous mixture was then added at 12 °C under nitrogen while stirring a solution of the substrate (2 mmol) in dioxane (~3 mL). After 30 min the reaction mixture was poured onto 20 mL of water and neutralized with 10% KOH. The solvents and unconverted substrate were removed by freeze-drying. The structural assignment of the resulting sulfonate(s) was based on ^1H NMR and mass spectrometry.

Kinetic Isotope Effect. The primary kinetic isotope effect was obtained for the monosulfonation of **1**-*2,7-d_2* which allows intramolecular H–D competition. In the ^1H NMR spectrum of the resulting sulfonates the peri and β protiums adjacent to the sulfo group are observed separately (see Figure 1), from which the ratio of the mono- and dideuteriomonosulfonic acids was determined. Accounting for the label content of **1**-*2,7-d_2* (see before), the k_H/k_D ratio was accordingly calculated to be 3.8 ± 0.3.

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