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AROMATIC SULFONATION XLVIII [1] : SIDE CHAIN SULFONATION OF meso-METHYLATED ANTHRACENES

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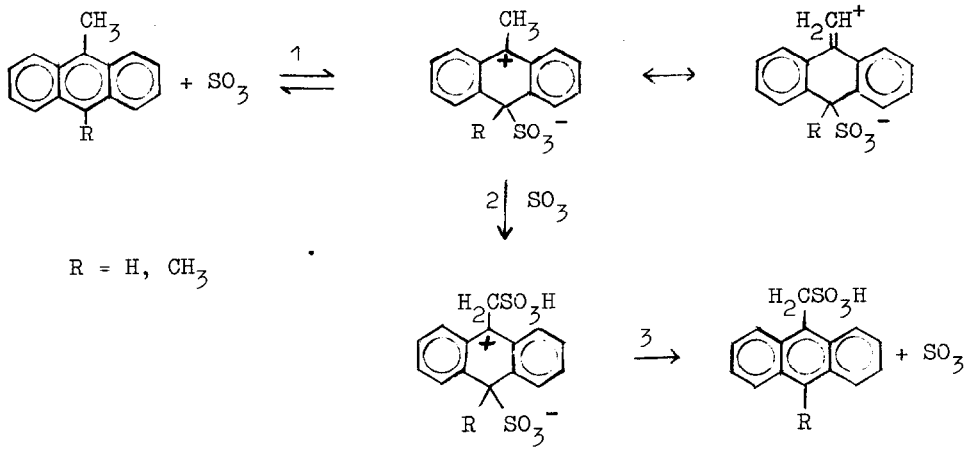
In the course of a study on the sulfonation of anthracene with dioxan-SO_3 [2], we have studied the sulfonation of 9-methyl- and 9,10-dimethyl-anthracene with that reagent.

9-Methylanthracene was sulfonated with 1.2 molar equivalents of dioxan-SO_3 in dioxan as solvent at 13-40°C for 18 hr. After quenching with water and neutralizing with sodium hydroxide 23% unconverted substrate was filtered off. The water of the filtrate was removed. The dried sodium sulfonate residue appeared to consist of a single compound $C_{15}H_{11}SO_3Na$; NMR (ppm), solvent DMSO-d_6 : δ 4.88 (2H,s), 7.49 (4H,m), 7.99 (2H,m), 8.44 (1H,s) and 8.47 (2H,m). Based on the elemental analysis and a comparison of the NMR data with those of the parent hydrocarbon (δ 3.03 (3H,s), 7.53 (4H,m), 8.05 (2H,m), 8.32 (2H,m) and 8.44 (1H,s)) in combination with those of phenylmethanesulfonic acid [3] and toluene, the compound was assigned to be sodium 9-anthrylmethanesulfonate. The presence of the methylene group was further proven by the occurrence of a triplet absorption (J=60 Hz) in the off resonance ^{13}C NMR spectrum of the sulfonate in DMSO-d_6 as solvent.

Similarly reaction of 9,10-dimethylanthracene with 1.2 molar equivalents of dioxan-SO_3 yields a mixture of 88% sodium 9-methyl-10-sulfomethylanthracene (δ 3.03 (3H,s), 5.00 (2H,s), 7.52 (4H,m), 8.32 (2H,m) and 8.55 (2H.m)) and 12% disodium 9,10-disulfomethylanthracene (δ 5.05 (s), 7.52 (m) and 8.55 (m)).

The methyl sulfonation may be explained by the following mechanism. It is



R = H, CH_3

presumed that the transfer of sulfur trioxide from dioxan to the meso-position of the methylanthracenes (step 1) is fast relative to a direct electrophilic sulfonation of the methyl hydrogen. With 9-methylanthracene this transfer will occur predominantly to the 10-position because of hyperconjugative electron release by the methyl group. This electron release enhances the acidity of the methyl hydrogens and renders them more susceptible towards electrophilic sulfonation (step 2). This step may proceed either by an S_E-2 mechanism or by initial proton loss and subsequent sulfur trioxide addition. Because of the electron withdrawing effect of the methylsulfonic acid substituent, the resulting σ-complex will lose sulfur trioxide with formation of the final product (step 3). The alternative possibility, i.e. loss of the proton, does not occur. In fact, the proton removing step in the formation of 9-anthracenesulfonic acid is very slow, because of steric hindrance between the incoming sulfonate group and the two peri-hydrogens at the positions 1 and 8. [2]

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