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SULTONE FORMATION IN THE SULPHONATION OF 9-tert-BUTYLANTHRACENE; AN UNUSUAL REARRANGEMENT OF THE SULTONE INVOLVING THE tert-BUTYL GROUP.[1]

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Recently we studied the aprotic sulphonation of a number of 9-alkylanthracenes which contained at least one α-hydrogen in the alkyl group.[2] We now report on 9-tert-butylanthracene (1) which behaves completely differently.

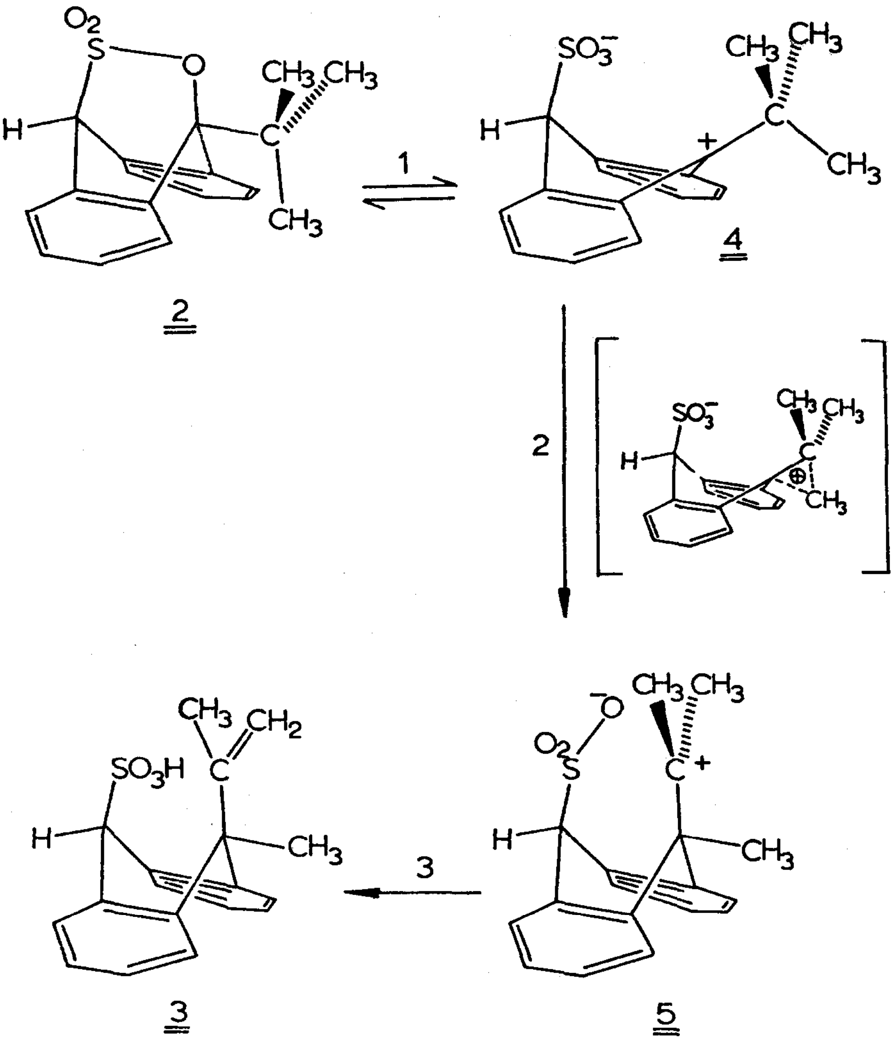
Compound 1 was prepared by dehydration of 9-tert-butyl-9-hydroxy-9,10-dihydroanthracene (obtained from anthrone and tert-butylbromide) with P_2O_5 (0.75 equiv., reaction time 5 min).[3] The sulphonation of 1 was carried out with 1 equiv. of the SO_3-dioxan complex in dioxan as solvent at 17°.[2,4] During the reaction a white precipitate was formed, which was filtered off, washed with dioxan and dried in vacuo at 35°. The compound was assigned to have structure 2 on the basis of the following evidence. I.r. (KBr, cm^{-1}): 1340 (s) and 1145 (s).[5] ^1H n.m.r. (DMSO-d_6; δ_H, ppm) 7.7-7.2 (m, 8H, aromatic H), 5.99 (s, 1H, S-C-H),[6] 1.73 (s, 3H, CH_3) and 1.17 (s, 6H, 2x CH_3). ^{13}C n.m.r. (DMSO-d_6; δ_C, ppm) 141.2, 133.5, 128.6, 128.5, 127.5, 126.3, 100.0, 67.4, 60.3, 24.9 and 19.6; off resonance for the aliphatic region: two singlets at 100.0 (C9) and 60.3 (C11), a doublet at 67.4 (C10), and two quartets at 24.9 and 19.6 (C12, C13, C14). Found: C 68.8; H 5.7; O 15.3; S 10.3. Calculated for $C_{18}H_{18}O_3S$: C 68.8; H 5.8; O 15.3; S 10.2.

Scheme 1

Compound 2 in DMSO-d_6 at 30° rearranged slowly (see Scheme 1). At 90° the conversion was complete in less than 30 min. The new product was assigned to be 3: I.r. (KBr, cm^{-1}): 1180 (s), 1025 (s), and 750 (m).[7] ^{1}H n.m.r. (DMSO-d_6, δ_H, ppm) 7.85-7.65 (m, 2H, aromatic H), 7.25-7.00 (m, 6H, aromatic H), 5.31 (s, 1H, vinylic H), 5.11 (s, 1H, S-C-$\underline{H}$), 5.05 (s, 1H, vinylic H), 1.47 (s, 3H, C$\underline{H}_3$) and 1,31 (s, 3H, C$\underline{H}_3$). ^{13}C n.m.r. (DMSO-d_6, δ_C, ppm) 151.4, 141.1, 131.3, 129.0, 126.7, 126.0, 124.4, 110.4, 63.6, 48.4, 36.0 and 21.6; off resonance for the non-aromatic carbons, two singlets at 151.4 (C11) and 48.4 (C9) with a small longe-range coupling with the hydrogens at C14 and C13 respectively, a doublet at 63.6 (C10), a triplet at 110.4 (C12) and two quartets at 36.0 and 21.6 (C14 and C13). Steric assignments were made on the basis of measurement of the nuclear Overhauser enhancement (NOE),[8,9] presuming that 3 has a non-planar boat structure similar to that of 9,10-dialkyl-9,10-dihydroanthracenes.[10] Irradiation of the singlet at δ_H=5.11 ppm (H10) gives a NOE (7%) on each of the *peri*-hydrogens (7.85-7.65, H4 and H5). Irradiation of the methyl singlet at δ_H=1.31 ppm gives a NOE (23%) on each of the other two α-hydrogens H1 and H8, the absorption of which is present in the multiplet at 7.25-7.00 ppm. No NOE could be observed on irradiation of the singlet at δ_H=1.47 ppm for any α-hydrogen. With the aid of double resonance it could be illustrated by the disappearance of the allylic coupling that the signal at δ_H=1.47 ppm is due to the hydrogens at C13. So the signal at δ_H=1.31 ppm is due to the hydrogens at C14. In view of these data we may conclude that the sulphonic acid and the 2-propenyl group are occupying the pseudo-axial positions. The rather small NOE (7%) on the α-aryl hydrogens upon irradiation of the H10 hydrogen may imply some "flattening" of the boat conformation.[11]

The unusual rearrangement of 2 into 3 may be explained in terms of the mechanism depicted in Scheme 2. The ^{1}H and ^{13}C n.m.r. data of 2 both show that (only) two methyls of the *tert*-butyl group are magnetically equivalent. This implies that the rotation around the C9-CMe$_3$ bond is restricted. From a study of molecular models it appears that the most likely conformation of 2 is as shown in Scheme 2.[12] The heterolytic bond cleavage of the sultone 2 leads to the 1,6-dipolar intermediate 4 with the positive charge on C9 (step 1). A 1,2-methyl shift of 4 yields 5 (step 2) which undergoes a proton shift from one of the two equivalent methyls to the sulphonate group to yield 3 (step 3). Step 2 is similar to that proposed for the conversion of one *tert*-butyl group into methyl in the nitration of 2,4,6-tri-*tert*-butylnitrobenzene.[13] In the present study no such products resulting from loss of the Me$_2$C fragment are observed.[14] The proton shift (step 3) may be intramolecular in view of the geometric orientation of the two equivalent methyls and the sulphonate group of 5.

Scheme 2


O2
S
O
H
CH3 CH3
C
CH3
2
1
SO3⁻
H
+
CH3 CH3
C
CH3
4
2
SO3⁻
H
CH3 CH3
C
⊕
CH3
⁻O
O2S
CH3 CH3
C+
H
CH3
5
3
CH3 CH2
SO3H
C
H
CH3
3

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