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Dimethylsulfonio- and sulfo-de-hydrogenation on reaction of azuleno[2,1,8-*ija*]azulene (isopyrene) with the dimethyl sulfoxide-sulfur trioxide complex as reagent ^{a,b}

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Abstract. Reaction of azuleno[2,1,8-*ija*]azulene (isopyrene, **1**) with SO₃ in the presence of an excess of DMSO leads mainly to mono-“dimethylsulfonio-de-hydrogenation” with formation of 5-(dimethylsulfonio)isopyrene, the amount of initial sulfonation being relatively small. Subsequently, the 5-(dimethylsulfonio)isopyrene is relatively slowly sulfo-de-hydrogenated to yield 5-(dimethylsulfonio)isopyrene-10-sulfonic acid.

Introduction

Our recent studies on the sulfonation of azuleno[2,1,8-*ija*]azulene (**1**), further to be referred to as isopyrene, with sulfur trioxide using traditional solvents like dichloromethane (DCM), nitromethane and dioxane, were found to be complicated by the low solubility of the substrate. The solubility of **1** is substantially larger in dimethyl sulfoxide (DMSO). In order to effect the homogeneous conversion of **1** we employed DMSO-SO₃ as reagent² both in DMSO and in DCM as solvent.

According to X-ray crystallographic^{4,5}, spectroscopic^{6–8}, and bond order⁹ evidence, isopyrene is a planar resonance hybrid to which the mesomeric structure **1a** is making the predominant contribution. Thus, in first approximation, **1** is a [14]annulene with a central bridging C=C moiety as a perturbation. Standard Hückel MO calculations showed the highest electron density to be at C(5) and C(10)⁹, predicting electrophilic attack to occur at these positions, as was in fact observed for protonation^{10,11a}, halogenation^{11b,12} and chloromercuriation¹³.

Results and discussion

The reaction of isopyrene (**1**) with the DMSO-SO₃ reagent was studied in both DMSO and DCM as solvents. The reaction mixtures proved to be homogeneous. The results are collected in Table I. The variation of the product

composition with the reaction time for the reaction of **1** in DMSO with 2.0 mol-equiv. of SO₃ at 25°C is shown in Figure 1. The main initial reaction taking place is not sulfo-de-hydrogenation, but – much to our surprise – dimethylsulfonio-de-hydrogenation. In fact, reaction of **1** in DMSO with 2.0 mol-equiv. of SO₃ at 25°C for 1.1 h leads to the formation of 61% of 5-(dimethylsulfonio)isopyrene (1-5-S⁺Me₂) with small amounts of isopyrene-5-sulfonic acid (1-5-S) (11%); further substitution furnishes 1-5-S⁺Me₂-10-S and 1-5,10-S₂, but no 1-5,10-(S⁺Me₂)₂ (entry 1a). By graphical extrapolation of the contents of the two initial products to the time region, in which the secondary products are still virtually absent (see Figure 1), the rate coefficient ratio $k(1 \rightarrow 1-5-S^+Me_2)/k(1 \rightarrow 1-5-S)$ was estimated to be 4.5 ± 0.5 . With 4.0 mol-equiv. of SO₃ in DMSO as solvent (entry 2), the rate of substrate conversion is higher, but the same type of products is observed. The optimal yields of 1-5-S⁺Me₂ are 77–78% (entries 1d and 2a). Upon quenching of the DMSO reaction mixtures with water and subsequent neutralization, the 1-5-S⁺Me₂ cation is partly converted into 5-(methylthio)isopyrene (1-5-SMe) (entries 1f and 3–5).

The dimethylsulfonio-de-hydrogenation of isopyrene (**1**) may be explained as follows (Scheme 1). Complexation between DMSO and SO₃ affords the dipolar dimethyl(sulfonato)sulfonium reagent which reacts as an electrophile with **1** to yield the dipolar 14 π aromatic σ -complex **2**, the positive charge of which is delocalized over all the fifteen C(sp²) carbons^{10,11a}. Subsequent intramolecular proton shift of the C(sp³)-bonded hydrogen in a favoured six-membered cyclic transition state affords the isopyrene derivative **3** which loses HSO₄[–] with formation of 1-5-S⁺Me₂. HS₂O₇[–] is a better leaving group than HSO₄[–]; accordingly the conversion of **3** into 1-5-S⁺Me₂ may proceed (in part) by initial addition of SO₃ to the S-O-S oxygen with formation of **4** and subsequent loss of HS₂O₇[–]. The further substitution of 1-5-S⁺Me₂ affords 1-5-S⁺Me₂-10-S and that of 1-5-S both 1-5,10-S₂ and 1-5-S⁺Me₂-10-S. The absence of 1-5,10-(S⁺Me₂)₂ among

^a Aromatic sulfonation 122. For part 121, see H. Cerfontain, A. Koeberg-Telder and U. Lerch, Recl. Trav. Chim. Pays-Bas 112, 584 (1993).

^b Following the recommendations for Nomenclature for organic chemical transformations¹, the names dimethylsulfonio-de-hydrogenation and sulfo-de-hydrogenation are preferred over dimethylsulfonio-de-protonation and sulfo-de-protonation, respectively.

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Table I Reaction of isoprene (1) with DMSO-SO₃.

Entry	Reaction conditions			Method of reaction and analysis	Reaction mixture composition (% ± 2) ^b										
	SO ₃ (mol-equiv)	Solvent ^a	T (°C)		t (h)	Unconv. substr.	1-5-S ⁺ Me ₂		1-5-SMe		1-5-SO ₃ X		1-5-S ⁺ Me ₂ -10-SO ₃ X		1-5,10-(SO ₃ X) ₂
							CD ₃	CH ₃	CD ₃	CH ₃	CD ₃	CH ₃	CD ₃	CH ₃	
1 a	2.0	DMSO-d ₆	25	1.1	20	61	-	-	-	11	6	-	2		
b				2.1	10	69				7	10		4		
c				4.5	3	75				5	13		4		
d				24	-	78				3	16		3		
e				54		75		-	-	3	18		4		
f				70 ^c		22		-	-	5	5		5		
2 a	4.0	DMSO-d ₆	25	0.5	-	77		63	-	3	15		5		
b				3.9		53				-	38		-		
c				24		17				7	39		-		
3	1.0	DMSO-d ₆ /DCM-d ₂ (1:10, v/v)	0	2.5 ^c	25	26		38	-	7	2				
4	2.0	DMSO-d ₆ /DCM-d ₂ (1:5, v/v)	0	2.5 ^c	-	79		13	-		6		2		
5	2.0	DMSO/DCM (1:64, v/v)	-20	4.0 ^c	70	-	10	-	19		-	1			

^a DMSO and DCM stand for dimethyl sulfoxide and dichloromethane, respectively. ^b X stands for H, unless the reaction mixture was quenched and neutralized; then X stands for K. ^c Reaction mixture obtained after quenching with water, subsequent neutralization and removal of the solvents.

the products is notable. The apparently very low reactivity of $1-5-S^+Me_2$ for further dimethylsulfinio-de-hydrogenation at C(10) may be ascribed to the substantial electronic repulsion that would result in the twice positively charged σ -complex for substitution at C(10) between the positive charges at the 5-dimethylsulfinio sulfur and the adjacent C(5)¹⁴, which carries a delocalized charge of the aromatic cationic moiety of the carbenium ion type of σ -complex^{11a,15}. The higher reactivity of $1-5-S^+Me_2$ for sulfo-de-hydrogenation than dimethylsulfinio-de-hydrogenation may be ascribed to the difference in the overall charge of the respective σ -complexes, that for the former conversion having a positive charge of one, and that for the latter conversion a positive charge of two. Somewhat related to the dualistic electrophilic behaviour of the DMSO- SO_3 reagent is the activation of an electrophile by the addition of SO_3 . The reaction of unsaturated compounds, like alkenes and diphenylethyne, with a weak electrophile XY is mediated by added SO_3 , as was in fact established by Zefirov and coworkers for ethyl nitrite¹⁶, phenylsulfenyl chloride¹⁷, chlorine¹⁸, *N*-chlorodiethylamine¹⁹ and *N,N*-dialkylbenzenesulfenamide²⁰ as electrophiles. The reaction may proceed by the steps (1)–(3) via the dipolar intermediate $X-Y^+-SO_3^-$,

Scheme 1. Mechanism of dimethylsulfinio-de-hydrogenation on reaction of isopyrene (1) with DMSO- SO_3 .

although Zefirov proposed that the essential intermediate in the activation is the entity $X-O-SO_2-Y$, formed from $X^{\delta+}-Y^{\delta-}$ by insertion of SO_3 .

Figure 1. Homogeneous reaction of isopyrene (1) with 2.0 mol-equiv. of SO_3 in $DMSO-d_6$ as solvent at $25^\circ C$; variation of product composition with reaction time. (●—●) 1; (○—○) $1-5-S^+Me_2$; (+—+—) $1-5-S$; (□—□) $1-5-S^+Me_2-10-S$; (×—×—×) $1-5,10-S_2$.

Table II ^1H -NMR data of isopyrene (1) and its products on reaction with DMSO-SO_3 .

Compound	Solvent	δ , ppm (mult., J , Hz) of H atoms at the listed positions					
		1	2	3	4	5	10
1	$\text{DMSO-}d_6$	9.00 ^a	8.41 ^a				
1-5-SO₃K	$\text{DMSO-}d_6$	9.00 (dd, 9)	8.40 (t)	8.45 (t)	9.56 (dd, 9)	8.35 (s)	8.32 (s)
1-5,10-(SO₃K)₂	$\text{DMSO-}d_6$	9.57 (m)	8.42 (m)				
	D_2O	9.53 (m)	8.66 (m)				
1-5-S⁺Me₂	$\text{DMSO-}d_6$	9.28 (d, 9.7)	8.64 (t)	8.77 (t)	9.40 (d, 9.9)	3.78 (s) ^b	8.46 (s)
1-5-S⁺Me₂-10-SO₃K	$\text{DMSO-}d_6$	9.78 (d, 9.8)	8.62 (t)	8.72 (t)	9.36 (d, 9)		
1-5-SMe	$\text{DMSO-}d_6$	9.04 (d, 8.8)	8.45 (t)	8.52 (t)	9.10 (d, 9.9)	2.62 (s) ^b	8.37 (s)

^a AA'/BB'-system. ^b Methyl ^1H -NMR signals of 1-5-S⁺Me₂ and 1-5-SMe are only present when the sulfonation was performed in non-deuterated DMSO (Table I, entry 5).

Table III ^{13}C -NMR spectra (solvent $\text{DMSO-}d_6$) of isopyrene (1) and its products on reaction with DMSO-SO_3 .

Compound	δ , ppm of C atoms at the listed positions									
	1	2	3	4	5	10	4a	9a	10b	Me-5
1	129.21	130.82			114.91		143.26		123.05	
1-5-SO₃K	129.68	131.05	131.12	130.10	132.7	114.93			121.35	
1-5,10-(SO₃K)₂	130.52	131.31			132.28				119.73	
1-5-S⁺Me₂	133.55	132.94	135.15	127.23	140.0	116.32	144.52 ^a	144.06 ^a	125.22	31.04
1-5-S⁺Me₂-10-SO₃K	134.06	133.02	135.33	127.53					123.7	
1-5-SMe	130.33	131.45	131.70	127.26	117.45	115.08	144.89 ^b	143.66 ^b	122.53	23.15

^{a,b} The assignments may be reversed.

Experimental

Isopyrene (**1**) was synthesized starting from 9,10-dihydroanthracene^{5,21}. The ^1H -NMR spectra were recorded on Bruker AC-200 and WM-250 spectrometers.

Sulfonation procedures

Method A. To a solution containing 0.05 mmol of **1** in 0.5 ml of $\text{DMSO-}d_6$ was added at 25°C with stirring the desired amount of the $\text{SO}_3\text{-DMSO-}d_6$ reagent (2.0 or 4.0 mol-equiv., *i.e.* 100 or 200 μl). This reagent was prepared by addition of 0.4 mmol of SO_3 under argon at 18°C with stirring to 0.38 μl of $\text{DMSO-}d_6$. The progress of the homogeneous reaction at 25°C was monitored by ^1H -NMR by recording spectra after appropriate time intervals. Ultimately the reaction mixture was worked up by pouring it upon 5 ml of ice-water and adding dilute aqueous KOH till the pH was between 7.5 and 8.5. The solvents of the resulting solution were subsequently removed by freeze-drying.

Method B. To a solution of 0.05 mmol of **1** in 0.5 ml of dichloromethane or dichloromethane- d_2 was added (at 0 or -20°C)

the appropriate amount of the $\text{SO}_3\text{-DMSO-}d_6$ reagent (for the preparation, see method A) and the dark-green heterogeneous reaction mixture stirred for the desired period of time at that temperature. The reaction mixture was quenched with ice-water and worked up as described in method A.

The various solid residues obtained after working up the reaction mixtures were dissolved in $\text{DMSO-}d_6$ or D_2O as appropriate, and the ^1H - and ^{13}C -NMR spectra recorded.

The structural assignments of the components of the reaction mixtures were made on the basis of the observed ^1H -NMR chemical shifts, absorption area ratios and coupling constants in combination with the ^1H -NMR shielding parameters of the SO_3H and SO_3^- substituents²². The ^1H - and ^{13}C -NMR assignments are compiled in Tables II and III²³.

The solid residues of the two product mixtures, listed in Table I as entries 4 and 5, were analyzed by fast-atom-bombardment (FAB) mass spectrometry by use of a Fisons 9Q double focussing hybrid instrument. The samples were dissolved in 3-mercapto-1,2-propanediol. Small droplets of these solutions were then put on the top of a stainless-steel probe and – in the ion source – bombarded with Xe atoms having an energy of 8 KeV. The results are compiled in Table IV. They show evidence for the presence in the mixtures not only of the species 1-5-S⁺Me₂, but also of 1-5-SMe, since fragmentation under the FAB conditions is limited.

Table IV Fast atom bombardment (FAB) mass spectral data of neutral product mixtures resulting from reaction of **1** with DMSO-SO_3 .

m/z		Relative peak intensity in product mixture ^{a-c}		Structural assignment
M^+	$[\text{M}+1]^+$	Entry 4	Entry 5	
269		100	–	1-5-S ⁺ (CD ₃) ₂
	270	12.9	–	
263		–	28.5	1-5-S ⁺ (CH ₃) ₂
	264	–	11.8	
251		25.3	–	1-5-SCD ₃] ⁺
	252	16.2	–	
248		–	34.7	1-5-SCH ₃] ⁺
	249	–	28.9	
233		16.9	24.9	1-5-S] ⁺
	234	4.2	7.3	
202		12.8	100	1] ⁺
	203	3.5	94.7	

^a The peak intensity data of a given product mixture are normalized to the base peak of M^+ . The reagent, solvent and any sulfonate ion peaks are of low intensity (<3% of the base peak) and are not listed. ^b No peaks corresponding with $[\text{M}+\text{K}]^+$ were observed.

^c The intensities of the $[\text{M}+1]^+$ peaks were corrected for the contributions due to ^2H , ^{13}C and ^{33}S .

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