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ARTICLE TYPE

Formation of Dications Bearing $S(OH)_2^+$ Group from Long-lived 9,9-Dimethyl-10-R-phenanthrenium Cations in $FSO_3H-SbF_5/SO_2ClF/SO_2$: A Mechanistic Study[†]

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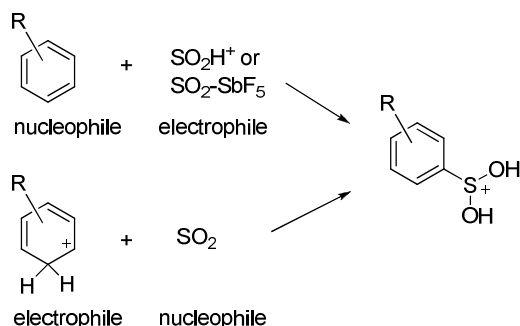
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¹H and ¹³C NMR studies have shown that the long-lived 9,9-dimethyl-10-R-phenanthrenium cations (R = PhC≡C, Me, OH) generated in $FSO_3H-SbF_5/SO_2ClF/SO_2/CD_2Cl_2$ transform into long-lived 7-dihydroxysulfonio-9,9-dimethyl-10-R-phenanthrenium dications. Effect of 10-R substituents on the reaction rate suggests that a key step in the reaction mechanism is addition of SO_2 to protonated phenanthrenium cations.

Introduction

It is known that aromatic compounds in superacids, such as $HF-SbF_5$ and FSO_3H-SbF_5 , containing SO_2 , transform into protonated sulfonic acids.¹⁻³ The mechanism of this reaction may consist in addition of SO_2 to arenium cations formed under protonation of aromatics or electrophilic attack of the cation SO_2H^+ or complex of SO_2 with SbF_5 on the aromatics involved in equilibrium with arenium ions.^{1,4}

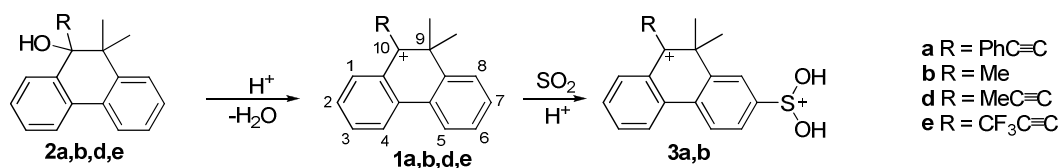


These mechanisms suggest the opposite effect of the substituent R on the reaction rate. While studying the long-lived 9,9-dimethyl-10-R-phenanthrenium cations^{5,6} we have found that these cations are convenient model structures for study of carbocation reactions mechanisms. In the present work we have used these cations to determine the mechanism of sulfination reaction.

Results and Discussion

We have found that the long-lived 9,9-dimethyl-10-

phenylethynylphenanthrenium cation (**1a**)⁵ generated from 9-hydroxy-10,10-dimethyl-9-phenylethynyl-9,10-dihydrophenanthrene (**2a**) (Scheme 1) in $FSO_3H-SbF_5/SO_2ClF/SO_2/CD_2Cl_2$ at $-95\text{ }^\circ\text{C}$, at $-71\text{ }^\circ\text{C}$ quickly ($t_{1/2} = 35\text{ min}$) and totally turns into another long-lived cationic particle. The structure of this particle, as unambiguously determined from 2D COSY, ROESY, HSQC and HMBC correlations (ESI, pp. S2-S6), corresponds to the structure of the original cation (**1a**) in which the atom H^7 is replaced with a substituent containing no carbon atoms. The ¹H NMR spectrum of the new particle (Fig. 1) shows an additional singlet signal at $\delta\ 9.43\text{ ppm}$ of 2H intensity area, which correlates via long range spin-spin coupling with the ¹³C NMR signal of C^7 in the 2D HMBC spectrum. The protons corresponding to this signal are involved in slow exchange with acid protons and the NOE cross-relaxation is observed between these protons and H^6 and H^8 signals. By analogy to the literary data^{1-3,7} according to which the protons of $S(OH)_2^+$ group in cations $Ar-S(OH)_2^+$ do not exhibit fast exchange with acidic media and show distinct signals with chemical shifts in the range $\delta\ 9.12-9.63\text{ ppm}$ we believe that the new signal in our case belongs to $S(OH)_2^+$ group and the new formed particle is 7-dihydroxysulfonio-9,9-dimethyl-10-phenylethynylphenanthrenium dication **3a** (Scheme 1). Additional evidences for its dicationic nature are downfield shifts of all signals in the ¹H NMR spectrum (Fig. 1), particularly of the signals of H^6 and H^8 , relative to that of the original cation (**1a**), and instability of its solutions containing lock substance CD_2Cl_2 at the temperatures above $-60\text{ }^\circ\text{C}$, cf. ref. 8. The remarkable features of the sulfination reaction are its high rate and practically full regioselectivity. The rate constant of dication **3a** formation is $4 \times 10^{-3}\text{ s}^{-1}$ at $-71\text{ }^\circ\text{C}$.



Scheme 1

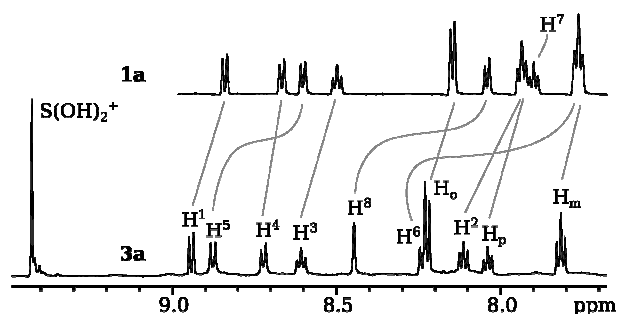
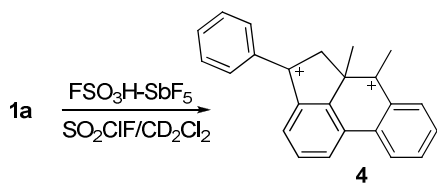


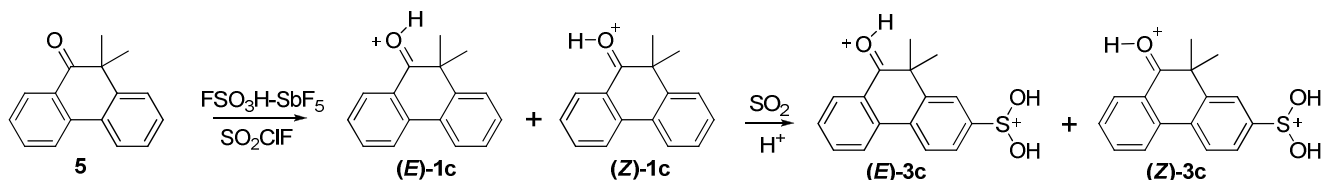
Fig. 1 ^1H NMR spectra (aromatics area) of cation **1a** in $\text{FSO}_3\text{H-SbF}_5/\text{SO}_2\text{ClF}/\text{CD}_2\text{Cl}_2$ at -91°C and dication **3a** in $\text{FSO}_3\text{H-SbF}_5/\text{SO}_2\text{ClF-SO}_2/\text{CD}_2\text{Cl}_2$ at -81°C .

If the same superacid system does not contain SO_2 , cation **1a** remains stable up to -40°C , at higher temperatures giving cyclization product dication **4** (Scheme 2).^{5b}



Scheme 2

An analogous sulfination reaction occurs with the long-lived 9,9,10-trimethylphenanthrenium cation **1b**⁹ (Scheme 1). At -71°C a mixture of this cation and 7-dihydroxysulfonio-9,9,10-trimethylphenanthrenium dication **3b** is formed (ESI, pp. S10-



Scheme 3

Sulfination of cation **1c** results in dication **3c** formation as the main product (ESI, pp. S18-S19). Dication **3c** also exists as an equilibrium mixture of slowly exchanging *E*- and *Z*-isomers (equilibrium constant Z/E is 0.4, exchange rate constant $Z \rightarrow E$ is 30 s^{-1} at -71°C). All the ^1H NMR signals of dication **3c** are downfielded relative to the corresponding signals of cations **1c**, the differences between ^1H NMR spectra of *E*- and *Z*-isomers being analogous to those observed for *E*- and *Z*-isomers of cation **1c**. In this case the sulfination reaction is slower than that of **1a**

S15), the content of the latter being 34%, and maintaining practically not increased upon standing or by adding an additional amount of SO_2 . As in the case of **3a**, all ^1H NMR signals of **3b** are downfielded relative to that of the precursor monocation **1b**. The downfield displacement of NMR signals of the phenanthrene fragment of **3b** is more pronounced than that of **3a** (ESI, p. S23), which is apparently due to lower opportunity for positive charge delocalization. Sulfination of **1b** proceeds faster than that of **1a**. The rate constant of dication **3b** formation measured at -100°C is $6 \times 10^{-4}\text{ s}^{-1}$ (0.2 s^{-1} for -71°C as recalculated using the Eyring equation).

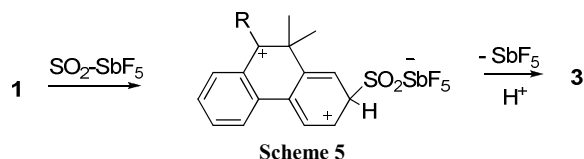
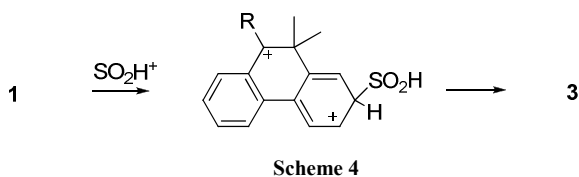
9,9-Dimethyl-10-hydroxyphenanthrenium cation **1c**¹⁰ (Scheme 3) also undergoes sulfination reaction (ESI, pp. S16-S17). This cation exists as a mixture of exchanging *E*- and *Z*-isomers (equilibrium constant Z/E is 0.3, exchange rate constant $Z \rightarrow E$ is 30 s^{-1} at -81°C). ROESY spectrum shows cross peaks due to NOE cross relaxation of hydroxyl proton with protons of methyl groups for the *E*-isomer, and with the H^1 proton for the *Z*-isomer. Hydroxyl proton of the *Z*-isomer is strongly downfielded relative to that of the *E*-isomer (δ 11.92 ppm vs 11.31 ppm) due to deshielding anisotropy of the aromatic ring. Significant chemical shifts difference for H^1 proton of *E*- and *Z*-isomers is observed (δ 8.73 ppm and 8.28 ppm, respectively). The probable reason of the downfield shift of H^1 of the *E*-isomer is its spatial proximity to the lone pair of oxygen atom, cf. ref. 11.

and **1b**. The rate constant of dication **3c** formation is $7 \times 10^{-5}\text{ s}^{-1}$ at -71°C .

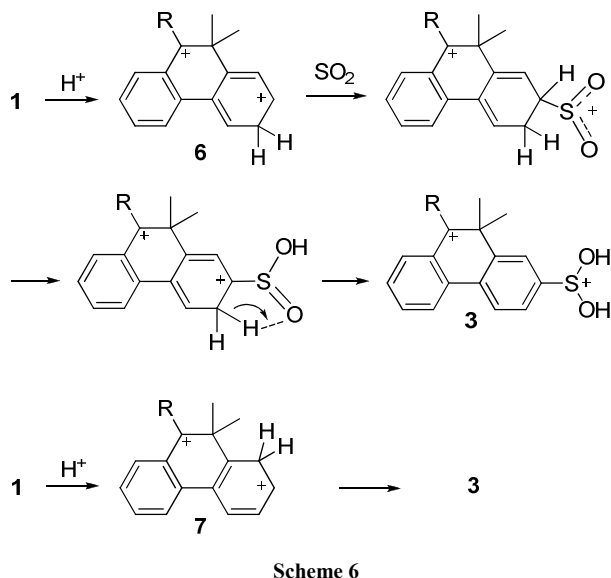
Both cations **1d** and **1e** (Scheme 1) do not yield observable amounts of sulfination products. Cation **1d**^{5a,6} at -71°C transforms into a complex mixture of unidentifiable products (ESI, p. S21). On the contrary, cation **1e**^{5a,6} is quite stable up to -39°C , content of the sulfination products being less than 2%. At higher temperatures this cation is decomposed (ESI, p. S22).

Possible mechanisms of the sulfinated dication formation are

presented in Schemes 4, 5 and 6, *cf.* refs. 1,4. The mechanism, in which the protonated SO₂ is an attacking electrophile (Scheme 4), seems to be unlikely, as this mechanism assumes an approach of two positively charged particles to the distance necessary for the formation of a chemical bond. In Scheme 5 complex SO₂·SbF₅¹² serves as electrophile. Its presence in the reaction mixture has been established by ¹⁹F NMR spectroscopy (ESI, p. S8), *cf.* ref. 13. Both Schemes 4 and 5 assume that cation **1** is a nucleophilic particle. The nucleophilicity of the aromatic fragment should be in line with the electron donating properties of 10-R substituent. Apparently the nucleophilicity should decrease in the order R = OH > CPh > Me. This assumption is confirmed by chemical shifts of aromatic fragments of cations **1a,b,c** in ¹H and ¹³C NMR spectra (ESI, p. S23). The rate of dication **3** formation according to Scheme 4 or 5, as determined by the nucleophilicity of cations **1**, would decrease in the order **3c** > **3a** > **3b**. However, the rate decreases just in the opposite order: **3b** > **3a** > **3c** (the rate constants ratio is approx. 50:1:0.02 at -71 °C). Moreover, neither of Schemes 4 and 5 can explain the observed regioselectivity of the reaction, as according to these mechanisms an electrophile has to attack the C⁷ atom bearing a partial positive charge.



Scheme 6 assumes that the superelectrophilic intermediates – dication **6** and/or **7** play a key role in the reaction. The inactivity of cation **1e** in the sulfonation reaction may result from a low concentration of the respective dication intermediates owing to low basicity of C⁸ and C⁶ atoms of cation **1e**.



In order to verify the possibility of intermediates **6** and **7** formation, we carried out the sulfonation reaction of **1a** in FSO₃D-SbF₅/SO₂ClF/SO₂ (ESI, p. S9). The methyl groups of both the precursor **1a** and the product **3a** do not undergo deuteration, as unambiguously follows from the absence of the corresponding signals in the ²H NMR spectrum. The ²H NMR signals in the aromatics region are too broad and indistinguishable from each others because of severe overlaps. Integrals of ¹H NMR signals of phenanthrene rings taken relative to the integrals of methyl group signals clearly indicate that protons belonging to the more positively charged ring (protons H¹⁻⁴ of both **1a** and **3a**) do not take part in deuteration to any visible degree. On the contrary, integrals of proton signals of the other phenanthrene ring both in the precursor monocation **1a** and in the sulfonated product **3a** (protons H⁵⁻⁸ of **1a** and protons H^{5,6,8} of **3a**) are significantly reduced due to their partial deuteration. Deuteration of **1a** into the positions H⁵⁻⁸ proceeds practically immediately even at -100 °C, i.e. much faster than sulfonation. Therefore dication **6** and **7** in superacid FSO₃H-SbF₅ can be intermediates in the sulfonation reaction. The regioselectivity of sulfonation can be explained by the higher stability of the dication sulfonated at C⁷ in comparison with other sulfonation products. In this case the second formal positive charge (at C⁷-S(OH)₂⁺) is located most distantly along the delocalized π bond system from the first one (at C¹⁰).

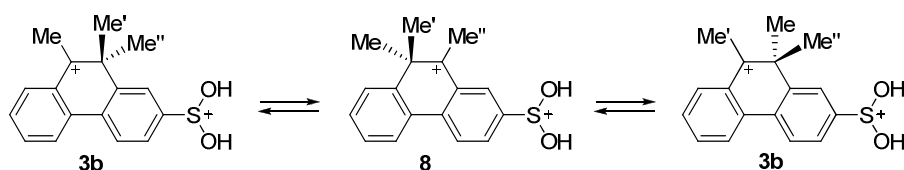
It is important to note that keeping the monocation precursors in FSO₃D in the absence of SbF₅ even up to -15 °C did not lead to any deuteration, and the reaction with SO₂ under these conditions also does not proceed. Therefore we believe that the role of SbF₅ in the sulfonation reaction consists solely in ensuring high acidity of the medium necessary for formation of the dication intermediates **6** and/or **7**.

In ¹H DNMR and ROESY spectra (ESI, pp. S14-S15) of dication **3b** chemical exchange between 9- and 10-methyl groups is observed (*k* = 6.4 s⁻¹ at -61 °C, DNMR), the signals of aromatic ring protons being intact. Probable mechanisms of this exchange are shown in Schemes 7 and 8. As the exchange rate between protons of S(OH)₂⁺ group of dication **3b** and protons of superacid medium (*k* = 0.2 s⁻¹ at -61 °C, ROESY, pseudomonomolecular approximation) is significantly less than the rate of methyl groups exchange, Scheme 8 cannot be the preferred one. The chemical exchange between 9- and 10-methyl groups of dication **3b** is slower than that of monocation **1b** (*k* = 12.3 s⁻¹ at -61 °C, DNMR) probably due to lower stability of the dication intermediate **8** (Scheme 7) compared to dication **3b**. In contrast to the latter monocation **1b** undergoes degenerate rearrangement, so that there is no such a retarding effect.

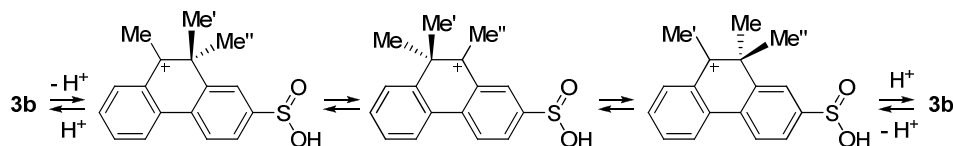
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Scheme 7



Scheme 8

5

Conclusions

Long-lived carbocations of the phenanthrene series are fruitful models for solving mechanistic problems of the organic reactions proceeding with formation of carbocation intermediates. The advantage of these models in study of the sulfination reaction is the opportunity to explore kinetics and mechanism of the reaction, based on dependence of the rate on the substituents in aromatic ring.

Experimental

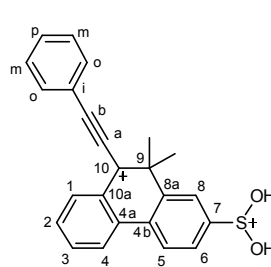
General methods and materials: NMR spectra were obtained at the Chemical Service Centre of Siberian Branch of the Russian Academy of Sciences on Bruker AV-600, using the residual proton and carbon signals of deuterated methylene chloride as internal references (CH_2Cl_2 , δ_{H} 5.33 ppm; CD_2Cl_2 , δ_{C} 53.6 ppm) and CFCl_3 (δ_{F} 0 ppm) as external standard. For structure elucidation and NMR signal assignment 2D correlation spectra ^1H - ^1H (COSY, ROESY) and ^1H - ^{13}C (HSQC, HMBC) were used.

Analysis of SO_2ClF was performed on Hewlett-Packard G1800A device, equipped with gas chromatograph HP 5890 of II series having capillary column HP-5MS and mass selective detector HP 5971. The column temperature was 30 °C.

Doubly distilled FSO_3H (b.p. 158-161 °C), freshly distilled SbF_5 , SO_2 (from $\text{Na}_2\text{S}_2\text{O}_5$ and H_2SO_4) drained by a transmission through conc. H_2SO_4 , and CD_2Cl_2 drained by 4Å molecular sieves were used. SO_2ClF was prepared by the method of Woyski.¹⁴ According to GC-MS data it contained SO_2 (8%). Pure SO_2ClF was obtained by distillation from SbF_5 .¹⁵

7-Dihydroxysulfonio-9,9-dimethyl-10-

phenylethynylphenanthrenium dication (3a). Solution of carbinol **2a**^{5a} (20 mg, 0.062 mmol.) in 0.12 mL of CD_2Cl_2 was added dropwise to solution of FSO_3H (130 mg, 1.3 mmol.) and SbF_5 (250 mg, 1.2 mmol.) in 0.3 mL of SO_2ClF - SO_2 (8% SO_2) placed into NMR tube under stirring at -95 °C. Formation of cation **1a**⁵ was observed. The tube was kept for 10 min at -71 °C



40 and then cooled down to -81 °C.

^1H NMR spectrum (δ , ppm): 2.13 s (6H, 9-Me), 7.82 t (2H, H_m , J 7.6 Hz), 8.04 t (1H, H_p , J 7.5 Hz), 8.11 t (1H, H^2 , J 7.6 Hz), 8.21-8.26 m (3H, H_o , H^6), 8.45 s (1H, H^8), 8.61 t (1H, H^3 , J 7.6 Hz), 8.72 d (1H, H^4 , J 8.7 Hz), 8.88 d (1H, H^5 , J 9.2 Hz), 8.94 d (1H, H^1 , J 8.2 Hz),

9.43 s (2H, OH). ^{13}C NMR spectrum: (δ , ppm): 31.7 q (9-Me), 52.2 s (C^9), 105.5 s (C_o), 119.8 s (C_i), 126.2 d (C^6), 126.3 d (C^8), 126.9 d (C^4), 128.7 d (C^5), 130.7 d (C_m), 133.5 d (C^2), 134.0 s (C^{4b}), 134.7 s (C^7), 135.5 s (C^{10a}), 138.1 d (C_o), 140.1 d (C_p), 140.1 d (C^1), 141.4 s (C^{4a}), 147.0 s (C^{8a}), 150.5 d (C^3), 161.2 s (C_b), 199.2 s (C^{10}).

Analogous NMR spectra were obtained for solution in SO_2 at -61 °C (ESI, p. S7). The signal of $\text{S}(\text{OH})_2^+$ group is observed at δ 9.86 ppm. ^{19}F NMR spectrum (δ , ppm): -101.8 d (4F, J 97 Hz), -134.9 quintet (1F, J 97 Hz) ($\text{SO}_2 \cdot \text{SbF}_5$). The ^{19}F NMR assignments were made using COSY ^{19}F - ^{19}F and the data of the paper.¹³

7-Dihydroxysulfonio-9,9,10-trimethylphenanthrenium

dication (3b). Solution of carbinol **2b**^{9b} (20 mg, 0.084 mmol.) in 0.12 mL of CD_2Cl_2 was added to solution of FSO_3H (115 mg, 1.15 mmol.) and SbF_5 (235 mg, 1.22 mmol.) in 0.25 mL of SO_2ClF - SO_2 (1:17 by volume) placed into NMR tube at -95 °C, the mixture was stirred and then warmed to -71 °C. Formation of the mixture of cation **1b**⁹ and dication **3b** was observed, the content of the latter being 34%. Addition of SO_2 (0.1 mL) to the solution did not result in increase of the content. ^1H NMR spectrum (δ , ppm): 2.01 s (6H, 9-Me), 3.65 s (3H, 10-Me), 8.16 t (1H, H^2 , J 7.7 Hz), 8.28 dd (1H, H^6 , J 8.8, 1.8 Hz), 8.58 d (1H, H^8 , J 1.8 Hz), 8.82 t (1H, H^3 , J 7.6 Hz), 8.89 d (1H, H^4 , J 8.1 Hz), 8.98 d (1H, H^5 , J 9.0 Hz), 9.03 d (1H, H^1 , J 8.3 Hz), 9.86 s (2H, OH). ^{13}C NMR spectrum: (δ , ppm): 27.8 q (9-Me), 26.7 q (10-Me), 54.6 s (C^9), 126.3 d (C^6), 127.0 d (C^8), 127.7 d (C^4), 129.4 d (C^5), 133.8 d (C^2), 133.5 s (C^{4b}), 135.7 s (C^7), 133.8 s (C^{10a}),

140.2 d (C¹), 145.1 s (C^{4a}), 145.2 s (C^{8a}), 156.0 d (C³), 239.9 s (C¹⁰).

7-Dihydroxysulfonio-9,9-dimethyl-10-

hydroxyphenanthrenium dication (**3c**). Solution of ketone **5**¹⁶ (20 mg, 0.090 mmol.) in 0.12 mL of CD₂Cl₂ was added to solution of FSO₃H (105 mg, 1.07 mmol.) and SbF₅ (230 mg, 1.06 mmol.) in 0.25 mL of SO₂ClF placed into NMR tube at -95 °C and the mixture was stirred. Formation of cation **1c**¹⁰ (as an equilibrium mixture of *E*- and *Z*-isomers) was observed by NMR.

Liquid SO₂ (0.05 mL) was added into the NMR tube, the resulting solution was mixed, kept at -70 °C for 5 h and then at -61 °C for 2 h. The reaction results in formation of a multicomponent mixture. The content of (*E*)-**3c** is approx. 35% and that of (*Z*)-**3c** is approx. 15%.

(*E*)-**1c** ¹H NMR spectrum (δ, ppm, -91 °C): 1.92 s (6H, 9-Me), 7.72 t (1H, H⁶, *J* 7.3 Hz), 7.82 t (1H, H⁷, *J* 8 Hz), 7.85 d (1H, H⁸, *J* 8 Hz), 7.85 t (1H, H², *J* 8 Hz), 8.44 t (1H, H³, *J* 7.7 Hz), 8.49 d (1H, H⁵, *J* 8.1 Hz), 8.61 d (1H, H⁴, *J* 8.5 Hz), 8.73 d (1H, H¹, *J* 8.1 Hz), 11.31 s (OH). ¹³C NMR spectrum: (δ, ppm, -91 °C): 27.6 q (9-Me), 46.8 s (C⁹), 121.4 s (C^{10a}), 125.5 d (C⁴), 125.9 d (C⁵), 126.0 s (C^{4b}), 127.3 d (C⁸), 129.5 d (C⁶), 130.7 d (C²), 133.2 d (C¹), 133.3 d (C⁷), 141.7 s (C^{8a}), 148.2 s (C^{4a}), 148.3 d (C³), 215.5 s (C¹⁰).

(*Z*)-**1c** ¹H NMR spectrum (δ, ppm, -91 °C): 1.96 s (6H, 9-Me), 7.88 d (1H, H⁸, *J* 7.9 Hz), 7.92 t (1H, H², *J* 7.5 Hz), 8.28 d (1H, H¹, *J* 8.1 Hz), 8.67 d (1H, H⁴, *J* 8.3 Hz), 11.92 s (OH); signals of H^{3,5,6,7} are hidden by multiplets of the respective signals of *E*-isomer. ¹³C NMR spectrum: (δ, ppm, -91 °C): 28.9 q (9-Me), 47.8 s (C⁹), 120.2 s (C^{10a}), 126.4 d (C⁴), 127.1 d (C⁸), 129.3 d (C¹), 129.3 d (C⁶), 130.8 d (C²), 133.4 d (C⁷), 142.4 s (C^{8a}), 147.6 d (C³), 147.9 s (C^{4a}), 217.0 s (C¹⁰); signals of C^{4b,5} are hidden by the respective signals of *E*-isomer.

(*E*)-**3c** ¹H NMR spectrum (δ, ppm, -91 °C): 2.00 s (6H, 9-Me), 8.04 t (1H, H², *J* 8 Hz), 8.24 d (1H, H⁶, *J* 9 Hz), 8.34 s (H⁸), 8.57 t (1H, H³, *J* 8 Hz), 8.71 d (1H, H⁴, *J* 8 Hz), 8.83 d (1H, H⁵, *J* 9 Hz), 8.86 d (1H, H¹, *J* 8 Hz), 9.72 s (2H, S(OH)₂), 12.22 s (OH). ¹³C NMR spectrum: (δ, ppm, -91 °C): 27.1 q (9-Me), 47.4 s (C⁹), 122.4 s (C^{10a}), 126.3 d (C⁸), 126.8 d (C⁴), 127.0 d (C⁶), 128.0 d (C⁵), 132.9 d (C²), 133.3 s (C^{4b}), 134.3 d (C¹), 134.9 s (C⁷), 142.8 s (C^{8a}), 143.5 s (C^{4a}), 148.6 d (C³), 216.1 s (C¹⁰).

(*Z*)-**3c** ¹H NMR spectrum (δ, ppm, -91 °C): 2.00 (9-Me), 8.10 (H²), 8.24 (H⁶), 8.36 (H⁸), 8.57 (H³), 8.75 (H⁴), 8.80 (H⁵), 8.47 (H¹), 9.71 (S(OH)₂), 12.82 (OH). The ¹³C NMR assignments for (*Z*)-**3c** are unavailable because of its low concentration.

Data on generation and attempts to sulfinate cations **1d,e** are given in ESI, p. S20.

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Notes and references

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