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Alkyl β-Oxoalkanesulfonates: Synthesis and Structure of Methyl Aroylmethanesulfonates

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Abstract—A number of new methyl esters of *para*-substituted benzoylmethanesulfonic acids was synthesized. An ability of both esters and salts to tautomeric transformations was examined. The esters were found to undergo an acid cleavage in alkaline medium.

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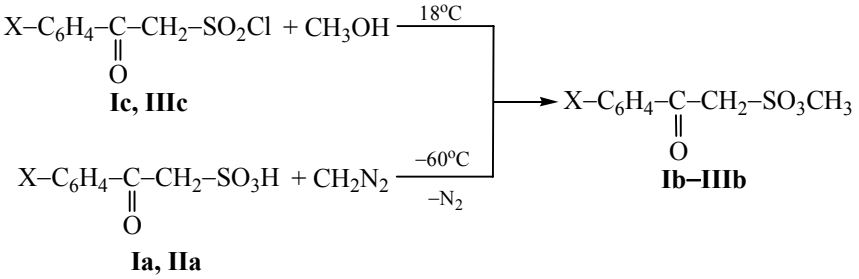
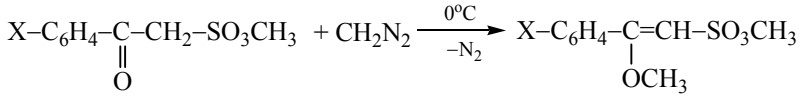
Previously we have proposed a new general synthetic method for methyl esters of β-oxoalkanesulfonic acids via the reaction of acetyl- and benzoylmethanesulfonic acids with diazomethane [1]. In this work we synthesized a series of new methyl esters of *p*-substituted benzoylmethanesulfonic acids **Ib**–**IIIb** and investigated their ability to tautomeric transformations and to the cleavage in an alkaline medium. The esters **Ib**–**IIb** were also obtained in another way: through the reaction of the previously unknown corresponding acid chlorides with methanol. Earlier only the salts of these sulfonic acids were described, and their chemical behavior was not studied [2].



X = *p*-CH_3 (**I**), *p*-OCH_3 (**II**), *p*-Cl (**III**).

As in the case of the previously studied benzoylmethanesulfonate [1], the analysis of the spectral characteristics of the presented acids and their esters suggests a high CH-acidity of both classes of compounds, which exceed those of the structurally similar β-oxocarboxylic acids and their esters (Table 1).

β-Oxocarboxylic acids esters are classical objects of studying the keto-enol tautomerism. As in the case of benzoylmethanesulfonate [1], in the UV and ^{1}H NMR spectra of the esters **Ib**–**IIIb** the presence of enol form was not detected regardless of the solvent polarity. However, like the carboxylic analogs, the studied esters decolorize a bromine methanol solution while standing and react with an excess of diazomethane like the enolized β-oxosulfones [3] to form methyl esters **IV**, **V**.



IIIb, IIb

X = Cl (**IV**), OCH_3 (**V**)

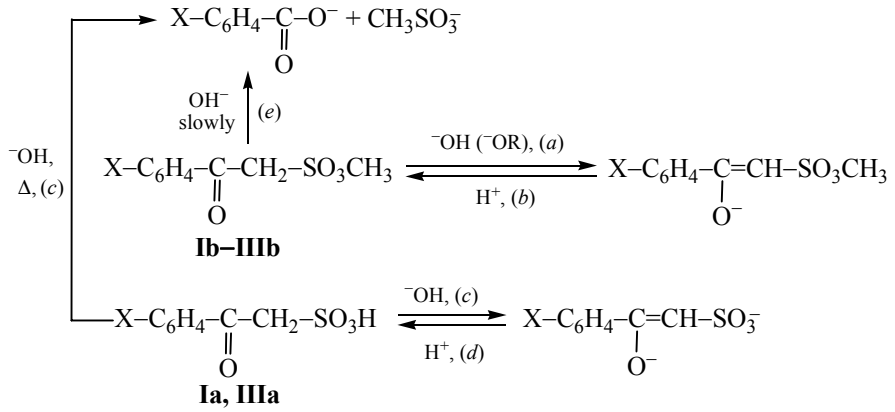
Table 1. Physicochemical characteristics of aroylmethanesulfonic acids and their esters **Ia**,**Ib**–**IIIa**,**IIIb**

$$p\text{-}XC_6H_4\text{–}\underset{\underset{O}{\|}}{C}\text{–}CH_2\text{–}SO_3Y$$

Comp. no.	X	Y	IR spectrum, ν, cm^{-1}			^1H NMR spectrum[a], δ_H, ppm (*J*, Hz)			
			SO_3	C=O	Ar	Solvent	CH_2	Ar	X
Ia	CH_3	H	1200 1060	1680	1580	$(CD_3)_2SO$	4.42 s	7.28 d 7.93 d (*J* 4)	2.47 s
Ib[a]	CH_3	CH_3	1370 1180	1680	1600	$CDCl_3$	4.59 s	7.11 d 7.69 d (*J* 4)	2.34 s
IIa	OCH_3	H	1200 1060	1680	1580	$(CD_3)_2SO$	4.41 s	6.86 d 7.89 d (*J* 5)	3.79 s
IIb[a]	OCH_3	CH_3	1370 1180	1675	1590 1570	$CDCl_3$	4.85 s	6.90 d 7.85 d (*J* 5)	3.83 s
IIIa	Cl	H	1200 1060	1680	1570	$(CD_3)_2SO$	4.48 s	7.72 d 8.19 d (*J* 4)	–
IIIb[a]	Cl	CH_3	1370 1180	1685	1580	$CDCl_3$	4.61 s	7.44 d 7.91 d (*J* 4)	–

[a] In the ^1H NMR spectra of compounds **Ib**–**IIIb** the signal of the protons of the methyl group of the SO_3CH_3 moiety was found as a singlet in the region of 3.89–3.90 ppm.

Methyl aroylmethanesulphonates are well soluble alkaline aqueous solutions. According to the spectral data, they form salts of the enolate structure (Table 2). In alkaline solution methyl aroylmethane-sulfonates are fully enolized as evidenced by the ^1H NMR and UV spectroscopy. According to the ^1H NMR spectra, the enolization of esters **Ib**–**IIIb** is observed in the presence of alkali: The signal of the methylene protons at 5 ppm disappears and the signal of the vinyl protons appears at 7.64 ppm. According to the UV spectra, this enolization is reversible: The acidification of an alkaline solution leads to disappearance of the absorption of enolate form and to an increase in the absorption of the oxoform (Table 2). Like the



(*a*) 5% NaOH solution (aq.) or NaOH in CH_3OH–$CHCl_3$; (*b*) acidification of the alkaline solution of ester; (*c*) 20% NaOH solution (aq.); (*d*) HCl; (*e*) 5% NaOH solution (aq.).

Table 2. The ^{1}H NMR and UV spectral data of methyl aroylmethanesulfonates **Ib**–**IIIb** in different media

p-XC_6H_4–C(=O)–CH_2–SO_3CH_3

Comp. no.	X	^{1}H NMR spectrum, δ_H, ppm (*J*, Hz)						UV spectrum, λ_{max}, nm (ε)[a]
		solvent	CH_3	CH_2	=CH	Ar	X	
Ib	CH_3	$CDCl_3$	4.38 s	5.08 s	–	7.68 d 8.20 d (*J* 8)	2.83 s	70% C_2H_5OH, 30% H_2O – 265 (1500) NaOH[b] – 231.5 (11700), 284 (12000) HCl[d] – 265 (13000)
		NaOD–CD_3OD[c]	3.40 s	–	7.63 s	7.43 d 7.85 d (*J* 8)	2.61 s	
IIb	OCH_3	$CDCl_3$	4.36 s	5.03 s	–	7.38 d 8.28 d (*J* 9)	4.26 s	70% C_2H_5OH, 30% H_2O – 226 (8000), 291 (16000) NaOH[b] – 245 (10000), 287 (16000) HCl[d] – 226 (7200), 292 (14400)
		NaOD–CD_3OD	4.06 s	–	7.64 s	7.11 d 7.91 d (*J* 9)	3.96 s	
IIIb	Cl	$CDCl_3$	4.38 s	5.13 s	–	7.88 d 8.31 d (*J* 8)	–	70% C_2H_5OH, 30% H_2O – 263 (16000) NaOH[b] – 234 (12800), 288 (10000) HCl[d] – 264 (14250)
		NaOD–CD_3OD	3.95 s	–	7.64 s	7.51 d 7.79 d (*J* 8)	–	

[a] UV spectrum of salts, λ_{max}, nm (ε): 20% NaOH–80% H_2O, 231 (6550), 278 (4040) (**Ia**); 228 (10000), 290 (7100) (**IIIa**); HCl, 266 (6000) (**Ia**); 265 (14000) (**IIIa**). [b] The solid alkali was added to a water–alcohol solution. [c] An alcoholic alkali solution was added to $CDCl_3$ solution. [d] The acidification of alkaline solution.

unsubstituted benzoylmethanesulfonate ester [1], esters **Ib**–**IIIb** in the course of time undergo acid cleavage as evidenced by the preparative isolation of the *para*-substituted benzoic acids in a yield of >90%. The decomposition rate depends on the nature of the substituents in benzene ring. According to the UV spectra (absorption intensity changes with time in the series OCH_3, H, Cl), the half-life decreases regularly (Table 3). This result, as well as the presence of an isobestic point in the electron spectra of esters **IIb**, **IIIb** taken over time is consistent with the assumption that the ketone form of β-oxocarboxylic esters undergoes the same acid cleavage.

Table 3. Change in UV spectra of methyl benzoylmethanesulfonate **IIb** and methyl aroylmethanesulfonate **IIIb** due to the acid cleavage in 5% NaOH (aq.)

p-XC_6H_4–C(=O)–CH_2–SO_3CH_3

Comp. no.	X	λ_{max}, nm (ε)	Half period τ, min	λ_{max}, nm (ε)
IIb	H	224 (9200) 278 (8500)	150	223.5 (8100) 278 (4200)
	OCH_3	248 (10000) 285 (16000)	210	248 (11000) 280 (8000)
IIIb	Cl	233 (11000) 283 (9600)	60	234 (11000) 281 (4600)

Aroylmethanesulfonic acids salts are also capable of enolization, but under more rigid conditions (20% alkaline aqueous solution). Unlike ester enolates, the generated dianions are stable and decompose only when boiled to form the decpmposition products, which are identified as the *para*-substituted benzoic acids.

EXPERIMENTAL

The ^{1}H NMR spectra were registered on a Tesla BS-487C spectrometer (80 MHz). The IR spectra were recorded on a UR-20 spectrometer from $CDCl_3$ solution or mullin mineral oil. Electronic spectra were recorded on a Specord M-40 spectrophotometer. The individuality of the compounds obtained and the

reaction progress were monitored by thin layer chromatography (TLC) on Silufol UV-254 plates eluting with a hexane–acetone mixture (1:2) and detecting with UV irradiation (254 nm). Synthesis of β-oxoalkanesulfonic acids **Ia**–**IIIa** was performed according to [2] via the sulfonation of fatty aromatic ketones obtained by acylating the corresponding benzene derivatives according to [4].

Methyl *p*-chlorobenzoylmethanesulfonate (IIIb). *a.* To a suspension of 5 g of *p*-chlorobenzoylmethanesulfonic acid in 30 ml of anhydrous ether was slowly added 30 ml of diazomethane in diethyl ether (*c* 0.00097 mol/ml) with cooling to –60°C and stirring. Then the temperature of the reaction mixture was gradually increased to 25°C. Diethyl ether was removed, and the residue was recrystallized from CCl_4. Yield 2.13 g (41%), mp 85–87°C. Found, %: C 43.50, H 3.67. $C_9H_9ClO_4S$. Calculated, %: C 43.46, H 3.62.

b. A mixture of 1.5 g of *p*-chlorobenzoylmethanesulfonyl chloride **IIIc** and 4 ml of methanol was kept for 1 h at 18°C and then cooled to 0°C. The precipitated crystals were filtered off and dried in air. Yield 1.21 g (83%), mp 85–87°C (CCl_4).

Methyl *p*-methoxybenzoylmethanesulfonate (IIb) was prepared similarly from 5 g of *p*-methoxybenzoylmethanesulfonic acid **IIa**. Yield 1.97 g (37%), mp 133–135°C (CCl_4). Found, %: C 52.55; H 5.50. $C_{10}H_{12}O_5S$. Calculated, %: C 49.18; H 4.09.

Methyl *p*-methylbenzoylmethanesulfonate (Ib) was prepared similarly from 1 g of *p*-methylbenzoylmethanesulfonyl chloride **Ic**. Yield 0.75 g (77%), mp 71–73°C (CCl_4). Found, %: C 52.63; H 5.26. $C_{10}H_{12}O_4S$. Calculated, %: C 52.75; H 5.50.

***p*-Chlorobenzoylmethanesulfonyl chloride (IIIc).** A mixture of 27 g of *p*-chlorobenzoylmethanesulfonic acid **IIIa** and 20 ml of PCl_3 was heated for 14 h on a water bath. Then, an excess of PCl_3 was removed, and the residue was recrystallized from $CHCl_3$. Yield 12.70 g (43%), mp 79–83°C. Found, %: C 38.09, H 2.49. $C_8H_6Cl_2O_3S$. Calculated, %: C 37.94, H 2.37.

***p*-Methylbenzoylmethanesulfonyl chloride (Ic)** was prepared similarly from 15 g of *p*- methylbenzoylmethanesulfonic acid **Ia**. Yield 3.1 g (19%), mp 65–71°C ($CHCl_3$). Found, %: C 46.29; H 4.09. $C_9H_9ClO_3S$. Calculated, %: C 46.45; H 3.87.

Methyl 2-methoxy-(*p*-chlorostyryl)sulfonate (IV). To a solution of 0.72 g of methyl *p*-chlorobenzoylmethanesulfonate **IIIb** in a mixture of 12 ml of anhydrous ether and 3 ml of anhydrous methanol was slowly added 11 ml of solution of diazomethane in diethyl ether (*c* 0.00097 mol/ml) with cooling to 0–5°C and stirring. Then, diethyl ether was distilled off, and the residue was chromatographed on a silica gel eluting with benzene. Yield 0.283 g (37%), oily substance. IR spectrum, ν, cm^{-1}: 1610 (C=C) 1590 (Ar), 1160, 1360 (SO_3). ^1H NMR spectrum, δ_H, ppm: 3.66 s (3H, OCH_3), 3.81 s (3H, SO_3CH_3), 5.79 s (1H, CH=), 7.34 m ($4H_{arom}$). Found, %: C 45.84; H 4.27. $C_{10}H_{11}ClO_4S$. Calculated, %: C 45.71; H 4.19.

Methyl 2-methoxy-(*p*-methoxystyryl) sulfonate (V) was prepared similarly from 0.8 g of methyl *p*-methoxybenzoylmethanesulfonate **IIb**. Yield 0.335 g (40%), oily substance. ^1H NMR spectrum, δ_H, ppm: 3.69 s (3H, OCH_3), 3.76 s (3H, OCH_3) 3.83 s (3H, SO_3CH_3), 5.68 s (1H, CH=), 6.83 d, 7.26 d ($4H_{arom}$). Found, %: C 51.24; H 5.56. $C_{11}H_{14}O_5S$. Calculated, %: C 51.16; H 5.43

Decomposition of *p*-chlorobenzoylmethanesulfonic acid (IIIa). A solution of 2 g of **IIIa** in 10 ml of 20% NaOH aqueous solution was heated for 5 h. After cooling to room temperature, the reaction mixture was acidified with hydrochloric acid to pH 1, the formed crystalline *p*-chlorobenzoic acid was filtered off. Yield 1.33 g (98%).

Decomposition of *p*-methylbenzoylmethanesulfonic acid **Ia** was performed similarly.

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