ISSN 1070-3632, Russian Journal of General Chemistry, 2014, Vol. 84, No. 12, pp. 2397–2400. © Pleiades Publishing, Ltd., 2014.
Original Russian Text © T.P. Efimova, E.S. Lipina, N.V. Kuz'mina, 2014, published in Zhurnal Obshchei Khimii, 2014, Vol. 84, No. 12, pp. 1979–1982.

Chemistry of β-Oxoalkanesulfonic Acids as CH-Acids

T. P. Efimova, E. S. Lipina, and N. V. Kuz'mina

Herzen State Pedagogical University of Russia, nab. r. Moyki 48, St. Petersburg, 191186 Russia
e-mail: kohrgpu@yandex.ru

Received September 16, 2014

Abstract—Ability of β-oxoalkanesulfonic acids and their esters to enter into the reactions characteristic for CH-acids (azocoupling, nitrosation, aldol condensation, Michael reaction) was demonstrated. New polyfunctional aliphatic sulfonic acids were synthesized as a result of these reactions.

Keywords: β-oxoalkanesulfonic acid, Michael reaction, aldol condensation, azocoupling, nitrosation

DOI: 10.1134/S107036321412007X

Due to the similarity of the structure of esters of β-oxoalkanesulfonic and β-oxocarboxylic acids a likelihood of their chemical behavior is expectable not only in alkaline media [1], but also in other reactions characteristic of CH acids. Data on the reactions of β-oxoalkanesulfonates involving the methylene group are very limited. Only coupling reaction of acetyl and benzoylmethanesulfonic acids with diazonium salts have been reported [2, 3], but the structure of the reaction products has not been discussed.

We first introduced methyl β-oxoalkanesulfonates into the azocoupling reaction. Alkyl sulfonates are moisture sensitive compounds that require application of an appropriate procedure. Therefore the azocoupling of methyl β-oxoalkanesulfonic acids **I–IV** with phenyldiazonium chloride was carried out in an aprotic medium in the presence of anhydrous potassium carbonate as a base. As a result the corresponding phenylhydrazones **VII–X** were obtained in good yields (up to 73%). Their structure was confirmed by NMR spectroscopy methods (see the table and Scheme 1).

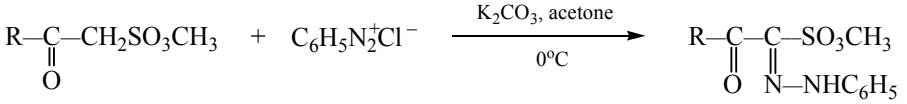
In the ^{1}H NMR spectra of aroyl derivatives **VIII–X** there were the proton signals of hydrazone form only. An exception is phenylhydrazone **VII**, in the ^{1}H NMR spectrum [$CDCl_3$, $(CD_3)_2CO$] of which there was a doubling of the signals of the protons of acetyl (2.39 and 2.51 ppm) and methylsulfonyl groups (3.84 and 3.99 ppm). The spectrum also contained the proton signals of NH- and OH-groups at 11.29 and 14.29 ppm, respectively. These data allows suggesting the presence of two tautomeric forms (azocompound and hydrazone) in a ratio of 1 : 2 (Scheme 2).

The absence of azoform in the case of methyl α-phenylhydrazonearoylmethanesulfonates **VIII–X** is possibly due to the stability of the aroyl moiety.

In the electronic spectra of compounds **VII–X** a strong long-wavelength maximum at 348–356 nm is observed, which characterizes the presence of an effective directed conjugation chain. IR spectra of these compounds contained strong absorption bands of all functional groups: sulfo (1345–1330, 1160–1140 cm^{-1}), C=O and C=N (1630–1660 cm^{-1}).

Of important synthetic interest is nitrosation of β-oxoalkanesulfonic acids. The reaction products can be converted into α-amino-β-hydroxyalkanesulfonic acids,

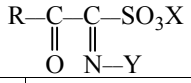
Scheme 1.



I–IV **VII–X**

R = CH_3 (**I, VII**), C_6H_5 (**II, VIII**), 4-Cl-C_6H_4 (**III, IX**), 4-CH_3-C_6H_4 (**IV, X**).

Physicochemical characteristics of compounds **VII–XII**



Como. no.	R	X	Y	^{1}H NMR spectrum ($CDCl_3$), δ, ppm			λ_{max} (CH_3CN), nm (ε)
				SO_3X	Y	R	
VII[a]	CH_3	CH_3	NH-C_6H_5	3.99 s 3.84 s	11.29 s 7.27 m	2.39 s 2.51 s	226 (8300) 348 (17600)
VIII	C_6H_5	CH_3	NH-C_6H_5	4.17 s	11.36 s 7.35 m	7.65 m	244 (14400) 356 (21000)
IX	*p*-Cl-C_6H_4	CH_3	NH-C_6H_5	4.15 s	11.40 s 7.04 m	7.64 d 7.26 d	244 (13300) 354 (19300)
X	*p*-CH_3-C_6H_4	CH_3	NH-C_6H_5	4.10 s	11.21 s 7.15 m	2.35 s 7.71 m	232 (13000) 352 (18300)
XI	C_6H_5	Na	OH	–	–	7.28–7.43 m[b]	258 (12250)[c]
XII	*p*-Cl-C_6H_4	Na	OH	–	–	7.71–7.98 m[d]	266 (13700)[c]

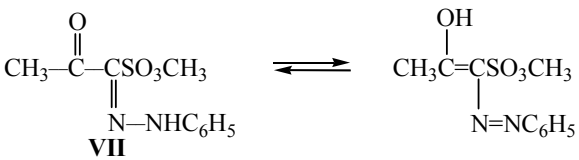
[a] In ^{1}H NMR spectrum along with the signal of NH group there was the singlet of OH groups at 14.20 ppm that indicated the presence of two tautomeric forms, hydrazone and azocompound, in a ratio of 1 : 2. [b] $[(CD_3)_2N]_3PO$. [c] 70% C_2H_5OH. [d] $(CD_3)_2SO$.

sulfo analogs of α-amino-β-hydroxycarboxylic acids. We first introduced methyl β-oxoalkanesulfonates **II–IV** into the nitrosation under conditions similar to those for esters of β-oxocarboxylic acids. Thus, the reaction of the corresponding methyl sulfonate with sodium nitrite in glacial acetic acid resulted in the formation of salts of α-oximino-β-oxosulfonic acids **XI–XIII** (Scheme 3). Spectral characteristics of the latter are given in the table.

In contrast to the coupling reaction, the nitrosation proceeded slowly under these conditions and was accompanied by hydrolysis of alkyl sulfonate. Unlike the starting esters, IR spectra of the obtained oximes contained the absorption bands of the salt sulfo group (1250–1220, 1080–1060 cm^{-1}), conjugated carbonyl (1680–1660 cm^{-1}), and C=N (1660–1645 cm^{-1}) groups.

Like esters of β-ketocarboxylic acids and unlike their salts, β-oxsoalkanesulfonates undergo the aldol condensation and Michael reaction.

Scheme 2.



VII

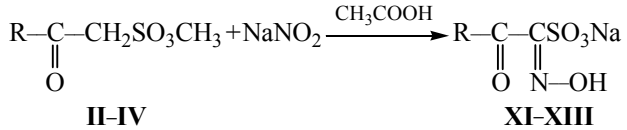
The condensation of benzoylmethanesulfonic acid **V** with aromatic aldehydes afforded new α-acylstyrylsulfonic acids **XIV** and **XV** (Scheme 4).

Reaction of β-oxoalkanesulfonates with nitroolefins is of interest as it allows the preparation of α,β-substituted γ-nitrosulfonates, precursors of β-arylhomotaurines with potential biological activity.

The reaction of ethyl benzoylmethanesulfoate **VI** with nitrostyrene resulted in the formation of adduct **XVI** (Scheme 5).

According to IR and ^{1}H NMR spectra the formation of nitrosulfonic esters was observed also in the case of *p*-chlorobenzoyl- and acetylmethanesulfonates permitting us to consider β-oxoalkanesulfonates as active donors in the Michael reaction.

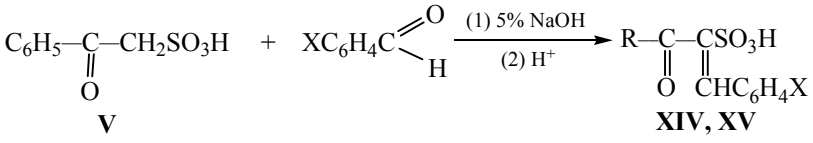
Scheme 3.



II–IV **XI–XIII**

R = C_6H_5 (**II, XI**), 4-Cl-C_6H_4 (**III, XII**), 4-CH_3-C_6H_4 (**IV, XIII**).

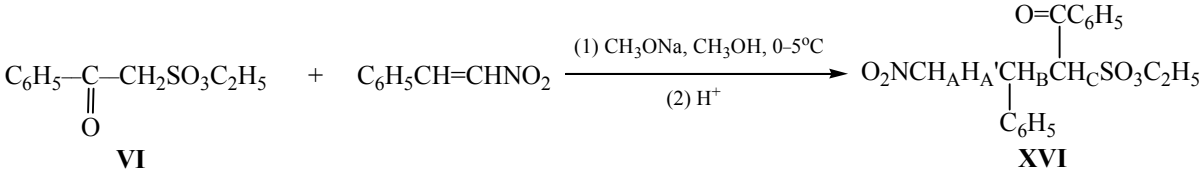
Scheme 4.



V **XIV, XV**

X = H (**XIV**), Cl (**XV**).

Scheme 5.



VI **XVI**

The structure of compounds **XIV**–**XVI** was confirmed by means of spectroscopy methods.

In summary, β-oxoalkanesulfonates can be used as CH-acids in diazotization, nitrosation, aldol condensation, and Michael reaction resulting in new polyfunctional aliphatic sulfonic acids.

EXPERIMENTAL

^{1}H NMR spectra were recorded on a Tesla BS-487C spectrometer (80 MHz). IR spectra were obtained on a UR-20 spectrometer in chloroform and mineral oil. Electronic spectra were registered on a Specord M-40 spectrophotometer. The reaction progress and individuality of the obtained compounds were monitored by TLC on Silufol UV-254 plates, eluting with a hexane–acetone mixture (1 : 2) and detecting with UV light (254 nm).

β-Oxoalkanesulfonic acids and their esters **I**–**VI** were synthesized according to procedures in [1, 4].

Methyl α-phenylhydrazoneacetylmethanesulfonate (VII). A mixture of 1 g of methyl acetylmethanesulfonate **I**, 2.37 g of anhydrous potassium carbonate, and 7 mL of anhydrous acetone was stirred for 0.5 h at room temperature. After cooling to 0–5°C, to the mixture was slowly added a cooled solution of phenyldiazonium chloride, obtained by diazotization of 0.88 g of aniline hydrochloride in 4 mL of 1.5 N HCl with a solution of 0.47 g of sodium nitrite in 3 mL of water. Then the reaction mixture was stirred for 10 min. The precipitate was filtered off and washed with water. Yield 1.7 g (97%), mp 104–105°C (hexane–carbon tetrachloride, 1 : 1). Found, %: C 47.00; H 4.85; N 11.14. $C_{10}H_{12}N_2O_4S$. Calculated, %: C 46.88; H 4.69; N 10.94.

Methyl α-phenylhydrazonebenzoylmethanesulfonate (VIII) was prepared similarly from 0.5 g of sulfonic ester **II**. Yield 0.5 g (72%), mp 125–127°C (hexane–carbon tetrachloride, 1 : 1). Found, %: C 56.67; H 4.57; N 8.93. $C_{15}H_{14}N_2O_4S$. Calculated, %: C 56.60; H 4.40; N 8.80.

Methyl α-phenylhydrazone(*p*-chlorobenzoyl)methanesulfonate (IX) was prepared similarly from 0.5 g of sulfonic ester **III**. Yield 0.5 g (73%), mp 139–141°C (hexane–carbon tetrachloride, 1 : 1). Found, %: C 51.12; H 3.75; N 7.96. $C_{15}H_{13}N_2O_4SCl$. Calculated, %: C 51.06; H 3.68; N 7.94.

Methyl α-phenylhydrazone(*p*-methylbenzoyl)methanesulfonate (X) was prepared similarly from 0.17 g of sulfonic ester **IV**. Yield 0.12 g (53%), mp 116–117°C (hexane–carbon tetrachloride, 1 : 1). Found, %: C 57.88; H 4.91; N 8.52. $C_{16}H_{16}N_2O_4S$. Calculated, %: C 57.83; H 4.82; N 8.43.

Sodium α-oximinobenzoylmethanesulfonate (XI). A solution of 0.69 g of sodium nitrite in 3 mL of water was slowly added to a mixture of 1 g of methyl benzoylmethanesulfonate **II** and 3 mL of glacial acetic acid within 1 h at stirring and cooling to 0°C. The reaction mixture was stirred for 2 h, and then evaporated to dryness. The residue was treated with hot ethanol. Sodium acetate was removed. Yield 0.48 g (60%), mp 160°C (decomp.). Found, %: C 38.17; H 2.49; N 5.60. $C_8H_6NO_5SNa$. Calculated, %: C 38.25; H 2.39; N 5.57.

Sodium α-oximino(*p*-chlorobenzoyl)methanesulfonate (XII) was prepared similarly from 1 g of

sulfonic ester **III**, 0.54 g of sodium nitrite, and 2.4 mL of glacial acetic acid. Yield 0.65 g (57%), mp 179°C (decomp.). Found, %: C 33.75; H 2.00; N 4.84. $C_8H_5NO_5SClNa$. Calculated, %: C 33.63; H 1.75; N 4.90.

Sodium α-oximino(*p*-methylbenzoyl)methanesulfonate (XIII) was prepared similarly from 0.5 g of sulfonic ester **IV**, 0.38 g of sodium nitrite, and 1.2 mL of glacial acetic acid. Yield 0.2 g (40%), mp 157°C (decomp.). Found, %: N 5.28. $C_9H_8NO_5SNa$. Calculated, %: N 5.18.

α-Benzoylstyrylsulfonic acid (XIV). A mixture of 1.7 g benzoylmethanesulfonic acid **V** and 0.9 mL of benzaldehyde in 20 mL of 5% aqueous sodium hydroxide solution was stirred at room temperature for 48 h. The reaction mixture was poured onto ice, acidified with HCl, and extracted with diethyl ether. The aqueous fraction was evaporated and the residue was recrystallized from methanol. Yield 0.5 g (21%), mp 265°C (decomp.). IR spectrum, ν, cm^{-1} (nujol): 1680 (C=O), 1640 (C=C), 1240, 1050 (SO_3). ^{1}H NMR spectrum (CD_3OD), δ, ppm: 7.45 s (1H, =CH), 7.45 m, 7.95 m ($10H_{arom}$).

α-Benzoyl(*p*-chlorostyryl)sulfonic acid (XV) was prepared similarly from 1 g of benzoylmethanesulfonic acid **V** and 0.7 g of *p*-chlorobenzaldehyde. Yield 0.4 g (23%), mp 275°C (decomp.). IR spectrum, ν, cm^{-1} (nujol): 1670 (C=O), 1630 (C=C), 1260, 1060 (SO_3). ^{1}H NMR spectrum $(CD_3)_2SO$, δ, ppm: 7.60 s (1H, =CH), 7.80 m, 8.25 m ($9H_{arom}$).

Ethyl 1-benzoyl-2-phenyl-3-nitropropane-1-sulfonate (XVI). A solution of 0.5 g of β-nitrostyrene in 17 mL of anhydrous methanol was slowly added to a solution of sodium ethylbenzoylmethanesulfonate **VI**, obtained by treating of 0.7 g of corresponding ester with sodium methoxide (0.069 g of sodium in anhydrous methanol, 7 mL), in 12 mL anhydrous methanol under stirring at 0°C. The reaction mixture was maintained at 18–20°C for 2 h, then poured onto ice, acidified with HCl (1 : 1) to pH 3–4, and extracted with diethyl ether. The organic fraction were dried over anhydrous $MgSO_4$ and evaporated. Yield 0.2 g (17%), mp 136–138°C (benzene–carbon tetrachloride, 1 : 3). IR spectrum, ν, cm^{-1} ($CHCl_3$): 1685 (C=O), 1590, 1445 (C_6H_5), 1560, 1370 (NO_2), 1355, 1170 (SO_3). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.27 s and 4.36 s (5H, $SO_3C_2H_5$), 4.58 d.d (1H, CH_B, $^3J_{BC}$ 11, $^3J_{BA}$ 5 Hz), 5.64 d (1H, CH_C, $^3J_{CB}$ 11 Hz), 4.96 d (1H, $CH_{A'}$, $^2J_{AA'}$ 13.5 Hz), 5.25 d.d (1H, CH_A, $^2J_{AA'}$ 13.5, $^3J_{AB}$ 5 Hz), 7.35 m ($5H_{arom}$). Found, %: C 57.29; H 5.04; N 3.71. $C_{18}H_{19}NO_6S$. Calculated, %: C 57.97; H 5.89; N 4.04.

REFERENCES

1. Efimova, T.P., Lipina, E.S., and Kuz'mina, N.V., *Russ. J. Gen. Chem*., 2013, vol. 83, no. 3, p. 462. DOI: 10.1134/S1070363213030092.
2. Parkes, G. and Tinsley, D., *J. Chem. Soc. Chem. Comm*., 1934, p. 1861.
3. Parkes, G. and Fisher, S., *J. Chem. Soc. Chem. Comm*., 1936, p. 83.
4. Efimova, T.P., Lipina, E.S., Berkova, G.A., and Pozdnyakov, V.P., *Zh. Org. Khim.*, 1996, vol. 32, no. 10, p. 1473.