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

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 1H NMR spectra of aroyl derivatives VIII–X there were the proton signals of hydrazone form only. An exception is phenylhydrazone VII, in the 1H NMR spectrum [CDCl3, (CD3)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-phenylhydrazoneacylmethanesulfonates 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, DOI: 10.1134/S107036321412007X

Scheme 1.

O

R–C–CH2SO3CH3 + C6H5N2Cl− K2CO3, acetone 0°C O N–NHC6H5

RI–IV

R = CH3 (I, VII), C6H5 (II, VIII), 4-Cl-C6H4 (III, IX), 4-CH3-C6H4 (IV, X).
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-ketocarboxylic 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-oxoalkanesulfonates undergo the aldol condensation and Michael reaction.

The condensation of benzoylmethanesulfonic acid V with aromatic aldehydes afforded new α-acetylstryryl-sulfonic 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 ¹H NMR spectra the formation of nitrosulfonic esters was observed also in the case of p-chlorobenzyol- and acetylmethanesulfonates permitting us to consider β-oxoalkanesulfonates as active donors in the Michael reaction.

### Scheme 3.

\[
\begin{align*}
\text{R} = & \quad \text{C}_6\text{H}_5 \quad (\text{II, XI}), 4\text{-Cl-C}_6\text{H}_4 \quad (\text{III, XII}), 4\text{-CH}_3\text{-C}_6\text{H}_4 \quad (\text{IV, XIII}).
\end{align*}
\]