## Reactions of Styryl and Phenylethynyl Sulfones with Some CH-Acids

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Abstract—Reactions of methyl and *p*-tolyl phenylethynyl sulfones with enolated of dimethyl malonate and malononitrile lead to the formation of sulfonyl-substituted derivatives of ethylidenemalonic acid. Methyl (E)- $\beta$ -styryl sulfone reacts with sodium enolates of dimethyl malonate, malononitrile, and methyl cyanoacetate to give common Michael adducts.

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It is known that  $\alpha,\beta$ -unsaturated sulfones are good Michael acceptors [1, 2]. For instance,  $\beta$ -(phenylsulfonyl) styrene reacted with sodium malonate and sodium malononitrile affording common Michael adducts [3, 4], and (methylsulfonyl)- and (phenylsulfonyl)ethenes in reactions with enolates of diethyl malonate, ethyl acetoacetate, ethylcyanoacetate, phenylacetonitrile, and nitroalkanes provide Michael adducts of the composition 2:1[5-7]. In some cases the Michael addition is accompanied with the 1,3-elimination of sulfinic acid leading to the formation of a cyclopropane derivative like in the reaction of  $\beta$ -(methylsulfonyl)- and  $\beta$ -(phenylsulfonyl) styrenes with the phenylacetonitrile enolate [4]. The information on reactions of ethynyl sulfones with CH-acids is scarce. However it is known that the (phenylsulfonyl)ethyne reacts with enolates of diethyl butylmalonate to give a common Michael adduct [8].

In this study we investigated the reactions of two ethynyl sulfones, 1-methylsulfonyl- and 1-*p*-tolylsulfonyl-2-phenylethynes (**I**, **II**) with dimethyl sodium malonate and sodium malononitrile. For comparison we also carried out the reactions of the same enolates and also of the methylcyanoacetate enolate with  $\beta$ -(methylsulfonyl) styrene (**III**). These reactions were performed in THF at 20–50°C using a slight excess of the reagent. The enolates were generated by treating the corresponding CH-acid with sodium hydride. From compound **III** after treating the reaction mixtures with water the expected Michael adducts **IVa–IVc** were isolated.



 $W = W' = CO_2Me(a), CN(b); W = CO_2Me, W' = CN(c).$ 

The reactions of ethynyl sulfones **I**, **II** with sodium malonate and sodium malononitrile afforded sulfonyl-substituted ethylidenemalonic acids **Va**, **Vb**, **VIa**, **VIb**.



R = Me(I, V), p-Tol (II, VI);  $W = CO_2Me(a), CN(b)$ .

Compounds **IV–VI** were isolated in the individual state by recrystallization in sufficient yields. Their structure was established from <sup>1</sup>H, <sup>13</sup>C NMR, and IR spectra.

The <sup>1</sup>H and <sup>13</sup>C NMR spectra confirm the presence in each compound **IV–VI** of diastereotopic W groups and diastereotopic protons of the  $CH_2$  fragment in compounds **IV**. The reaction of compound **III** with methyl cyanoacetate might result in the mixture of diastereomeric adducts **IVc**, but only one of them of unidentified configuration was obtained.



The formation of derivatives of ethylidenemalonic acid **V**, **VI** in the reactions involving ethynyl sulfones **I**, **II** is apparently due to the isomerization of the initially formed vinyl carbanion **A** into more stable allyl type anion **B** through the 1,3-proton shift from the CHW<sub>2</sub> fragment of the high CH-acidity. At quenching the reaction mixtures with water the protonation of **B** carbanion occurs at the harder reaction center, cf. [9].

Examples of similar reactions of CH-acids with some acetylene activated with the other acceptor moieties have been published [10–12].

## **EXPERIMENTAL**

<sup>1</sup>H and <sup>13</sup>C NMR spectra were registered on a spectrometer Bruker AMX-400 (400.1 and 100.6 MHz respectively) from solutions of compounds in CDCl<sub>3</sub>. IR spectra were recorded on a Fourier spectrophotometer InfraLYuM FT-02 from pellets with KBr. The purity of compounds was checked by analytic TLC on Silufol UV-254 plates, eluent hexane–diethyl ether, 2 : 1; development in iodine vapor.

**Reaction of ethynyl sulfones I, II with dimethyl malonate and malononitrile. General procedure**. The 60% dispersion of NaH in mineral oil (0.15 g, 3.8 mmol) was washed with hexane. The solvent was decanted, the residual solvent was evaporated in a vacuum. To the evacuated reactor argon was added till atmospheric pressure, 5 ml of THF was charged. The solution of 3.4 mmol of dimethyl malonate or malononitrile in 5 ml of THF was added dropwise while stirring within 10 min at 20°C under an argon atmosphere. The reaction mixture was stirred for 1.5 h, then at stirring and external cooling with running water to the reaction mixture was slowly added a solution of 3.1 mmol of ethynyl sulfone I [13] or II [14] in 10 ml of THF. The mixture was stirred

over 10 h at 50°C in the case of dimethyl malonate and 18 h at 20°C in event of malononitrile, afterwards it was diluted with water (250 ml) and netralized with dilute (1 : 1) HCl. The solid reaction product was filtered off, washed with water on the filter, dried in air, and rystallized from the mixture benzene–hexane.

**Dimethyl 2-[2-(methylsulfonyl)-1-phenylethylidene] malonate (Va).** Yield 33%, mp 83–84°C. IR spectrum, *v*, cm<sup>-1</sup>: 1740 s, 1732 v.s, 1725 v.s, 1717 s, 1435 m, 1316 s, 1235 s, 1130 m, 1096 m, 702 w. <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 2.86 s (3H, SO<sub>2</sub>Me), 3.50 s (3H), 3.83 s (3H, OMe), 4.83 s (2H, CH<sub>2</sub>), 7.28–7.35 m (2H<sub>arom</sub>), 7.37–7.43 m (3H<sub>arom</sub>). <sup>13</sup>C NMR spectrum,  $\delta$ , ppm: 41.9 (SO<sub>2</sub>Me), 52.4 (OMe), 52.8 (OMe), 59.0 (CH<sub>2</sub>), 127.4 (2C), 128.7 (2C), 129.7, 130.8, 137.8, 145.9 (C<sub>arom</sub>, C<sub>olefin</sub>), 163.8, 165.8 (C=O). Found, %: C 53.91; H 5.22. C<sub>14</sub>H<sub>16</sub>O<sub>6</sub>S. Calculated, %: C 53.84; H 5.16.

**2-[2-(Methylsulfonyl)-1-phenylethylidene]** malononitrile (Vb). Yield 28%, mp 120–121°C. Spectral characteristics coincide with those published in [9].

**Dimethyl 2-[2-(***p***-tosyl)-1-phenylethylidene]malonate (VIa)**. Yield 69%, mp 122–123°C. IR spectrum, *v*, cm<sup>-1</sup>: 1740 s, 1732 v.s, 1319 m, 1258 m, 1227 s, 1142 m, 548 m. <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 2.40 s (3H, Me), 3.47 s (3H, OMe), 3.71 s (3H, OMe), 4.93 s (2H, CH<sub>2</sub>) 7.27 d (2H, *J* 8.1 Hz), 7.30 br.s (5H), 7.72 d (2H<sub>arom</sub>, *J* 8.1 Hz). <sup>13</sup>C NMR spectrum,  $\delta$ , ppm: 21.5 (Me), 52.3 (OMe), 52.5 (OMe), 59.8 (CH<sub>2</sub>), 127.5 (2C), 128.4 (4C), 129.2, 129.6 (2C), 136.3, 138.1, 144.5, 144.7 (C<sub>arom</sub>, C<sub>olefin</sub>); 163.6, 166.0 (C=O). Found, %: C 61.91; H 5.23. C<sub>20</sub>H<sub>20</sub>O<sub>6</sub>S. Calculated, %: C 61.84; H 5.19.

**2-[2-(***n***-Tosyl)-1-phenylethylidene]malononitrile (VIb)**. Yield 55%, mp 86.5–87.5°C. IR spectrum, *v*, cm<sup>-1</sup>: 2234 w, 1327 v.s, 1307 m, 1150 s, 1088 m, 741 m, 714 m, 694 m, 563 m, 528 m, 505 m. <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 2.43 s (3H, Me), 4.67 s (2H, CH<sub>2</sub>), 7.30 d (2H, *J* 8.0 Hz), 7.42–7.57 m (5H), 7.66 d (2H<sub>arom</sub>, *J* 8.0 Hz). <sup>13</sup>C NMR spectrum  $\delta$ , ppm: 21.7 (Me), 63.1 (CH<sub>2</sub>), 89.7, 163.9 (C<sub>olefin</sub>), 111.8, 112.0 (CN), 128.3 (4C), 129.2 (2C), 130.2 (2C), 132.8, 133.1, 134.8, 146.2 (C<sub>arom</sub>). Found, %: C 67.11; H 4.44; N 8.59. C<sub>18</sub>H<sub>14</sub>N<sub>2</sub>O<sub>2</sub>S. Calculated, %: C 67.06; H 4.38; N 8.69.

Reaction of ethenyl sulfone III with dimethyl malonate, malononitrile, and methyl cyanoacetate. General procedure. From 6.1 mmol of dimethyl malonate, malononitrile, or methyl cyanoacetate and 8.3 mmol of 60% dispersion of NaH in mineral oil the solution was prepared of sodium enolate in 10 ml of THF as described above. Then the solution of 5.5 mmol of ethenyl sulfone III [9] in 10 ml of THF was added. The mixture was stirred for 10 h at

50°C in the case of dimethyl malonate and 20 h at 20°C in the case of malononitrile and methyl cyanoacetate. Afterwards the reaction mixture was worked up as described above.

**Dimethyl 2-[2-(methylsulfonyl)-1-phenylethyl] malonate (IVa)**. Yield 22%, mp 120–121°C (benzene– hexane). IR spectrum, v, cm<sup>-1</sup>: 2955 s, 2932 s, 1748 v.s, 1732 s, 1431 w, 1300 s, 1254 s, 1154 s, 1123 s, 710 m, 517 s. <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 2.40 s (3H, SO<sub>2</sub>Me), 3.54 s (3H, OMe), 3.76 s (3H, OMe), 3.54–3.65 m (2H, CH<sub>2</sub>SO<sub>2</sub>), 3.83 d (1H, CHCO<sub>2</sub>Me, *J* 8.8 Hz), 4.04 t.d (1H, CHPh, *J* 3.5, 9.0 Hz), 7.25–7.44 m (5 H<sub>arom</sub>). <sup>13</sup>C NMR spectrum,  $\delta$ , ppm: 40.5,41.7, 52.6, 52.9, 56.6, 58.0, 128.3, 128.4 (2C), 129.0 (2C), 137.6 (C<sub>arom</sub>), 167.2, 167.8 (C=O). Found, %: C 53.54; H 5.81. C<sub>14</sub>H<sub>18</sub>O<sub>6</sub>S. Calculated, %: C 53.49; H 5.77.

**2-[2-(Methylsulfonyl)-1-phenylethyl]malononitrile** (**IVb).** Yield 46%, mp 132–133°C (benzene–hexane). IR spectrum, *v*, cm<sup>-1</sup>: 3025 w, 2894 m, 2260 w, 1412 m, 1300 s, 1265 m, 1142 v.s, 968 m, 787 m, 702 m, 502 m. <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 2.87 s (3H, SO<sub>2</sub>Me), 3.58 d.d (1H, *J* 4.9, 14.4 Hz), 3.72 d.d (1H, CH<sub>2</sub>, *J* 9.0 and 14.4 Hz), 3.98–4.05 m (1H, C<u>H</u>Ph), 4.78 d [1H, CH(CN)<sub>2</sub>, *J* 4.9 Hz], 7.41–7.47 m (2H<sub>arom</sub>), 7.47–7.55 m (3H<sub>arom</sub>). <sup>13</sup>C NMR spectrum,  $\delta$ , ppm: 29.1, 39.8, 42.1, 55.4; 111.0, 111.1 (CN); 128.0 (2C), 129.7 (2C), 130.0, 134.3 (C<sub>arom</sub>). Found, %: C 58.11; H 4.66; N 11.37. C<sub>12</sub>H<sub>12</sub>N<sub>2</sub>O<sub>2</sub>S. Calculated, %: C 58.05; H 4.87; N 11.28.

**Methyl 2-cyano-4-(methylsulfonyl)-3-phenylbutanoate (IVc)**. Yield 26%, mp 97–98°C (ethyl acetate– hexane). IR spectrum, v, cm<sup>-1</sup>: 2932 w, 2253 w, 1752 m, 1740 s, 1296 v.s, 1254 s, 1142 s, 934 m, 764 w, 513 w. <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 2.77 s (3H, SO<sub>2</sub>Me), 3.56 d.d (1H, J5.8, 14.4 Hz), 3.69 d.d (1H, CH<sub>2</sub>, J8.3, 14.4 Hz), 3.67 s (3H, OMe), 4.12–4.19 m (1H, C<u>H</u>Ph), 4.48 d (1H, CHCN, J5.3 Hz), 7.39 br.s (5H, Ph). <sup>13</sup>C NMR spectrum,  $\delta$ , ppm: 39.0, 42.0, 43.4, 53.5, 56.7, 114.7 (CN), 128.0 (2C), 129.1, 129.2 (2C), 135.8 (C<sub>arom</sub>), 164.4 (C=O). Found, %: C 55.41; H 5.66; N 5.07. C<sub>13</sub>H<sub>15</sub>NO<sub>4</sub>S. Calculated, %: C 55.50; H 5.37; N 4.98.

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