Michael Addition of *p*-Styrenesulfinate to Acrylic Compounds

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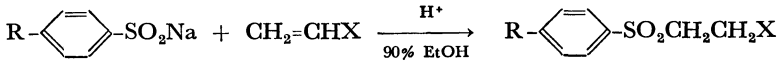
Synopsis. Acrylic compounds CH_2=CHX, where X represents -COOH, $-CONH_2$, -CN, and $-COOCH_2CH_2OH$, were converted into the corresponding 3-(*p*-vinylphenylsulfonyl)- and 3-(*p*-tolylsulfonyl)propionic acids and their derivatives by the Michael addition with *p*-styrene- and *p*-toluenesulfinates, respectively, in the presence of acid as proton source.

In the course of studies on the syntheses of functional vinyl monomers and polymers by the application of the nucleophilic reactions of *p*-styrenesulfinate and its polymer, a number of reactions were reported including simple displacement with halides, reductive addition to quinonoid compounds, and replacement of aromatic nitro group.[1)]

In this note, we wish to report the Michael addition of sodium *p*-styrenesulfinate and its model compound, *p*-toluenesulfinate, to acrylic compounds. A paper describing the Michael addition of arenesulfinates such as *p*-toluenesulfinate to α,β-unsaturated ketones such as methyl vinyl ketone in the presence of acid as proton source[2)] prompted us to undertake this study.

By use of acid either as Michael acceptor itself or as simple proton source we have synthesized a number of novel Michael addition products not obtained under conventional alkaline conditions as follows.



1a: R=CH_2=CH- **1b**: R=CH_3

2a: X=-COOH **2b**: X=$-CONH_2$ **2c**: X=-CN **2d**: X=$-COOCH_2CH_2OH$

3a: R=CH_2=CH-; X=-COONa **3b**: R=CH_2=CH-; X=$-CONH_2$ **3c**: R=CH_2=CH-; X=-CN **3d**: R=CH_2=CH-; X=$-COOCH_2CH_2OH$

4a: R=CH_3; X=-COONa **4b**: R=CH_3; X=$-CONH_2$ **4c**: R=CH_3; X=-CN **4d**: R=CH_3; X=$-COOCH_2CH_2OH$

It was found that acrylic Michael acceptors employed (**2a—d**) reacted with arenesulfinates (**1a—b**) at room temperature in the presence of an acid. The kind of R considerably affects both yield and mp of product (Table 1). However, weight losses during the course of isolation of products were greater in the case of **3a—d** than in the corresponding **4a—d**; no exact discussion can be made on the yield.

Use of the Michael addition gave rise to easy conversion of the acrylic double bond of a functional monomer to the 2-(*p*-vinylphenylsulfonyl)ethyl group, keeping the functional portion intact. Novel monomers **3a—d** thus synthesized may indicate polymerization behavior differing from that of **2a—d** leading to vinyl polymers with longer side chains, the terminal functional groups of which are more accessible.

Table 1. Yield of Michael-addition products

Compd	Yield/%[a)]	Mp/°C	AcOH
3a	38	179—180	none
3b	20	123—126	added
3c	38	87— 88	added
3d	63	liquid	added
4a	76	300<	none
4b	50	166—168	added
4c	80	93— 96	added
4d	77	liquid	added

a) For products isolated and purified, when required, after 12 h-reaction at room temperature.

Experimental

The infrared, ^{1}H-NMR, and mass spectra were recorded on a Hitachi 215 spectrophotometer, a JNM-PMX 60 spectrometer, and a Hitachi RMU-6 MG spectrometer, respectively, under standard conditions. The elemental analyses were carried out using a Perkin-Elmer 250 instrument.

*Sodium 3-(*p*-Vinylphenylsulfonyl)propionate (**3a**).* A solution of sodium *p*-styrenesulfinate (**1a**; 1.9 g, 10 mmol), synthesized according to the procedure reported,[1)] and acrylic acid (**2a**; 0.72 g, 10 mmol) in 90% ethanol (20 ml) was stirred at room temperature (20 °C) for 12 h to afford a pale pink precipitate, analytically pure without further purification. Found: C, 50.23; H, 4.38%. Calcd for $C_{11}H_{11}O_2SNa$: C, 50.38; H, 4.23%. IR (KBr) 2920, 2850 (CH_2), 1630 (vinyl), 1600 ($-COO^-$, Ar), 1305, 1140 (SO_2), 990, 910 (vinyl) cm^{-1}; NMR (DMSO-d_6+$CDCl_3$) δ 2.5 (t, 2H, CH_2), 3.5 (t, 2H, CH_2), 5.5 (d, 1H, $C\underline{H}_2$=CH–), 6.0 (d, 1H, $C\underline{H}_2$=CH–), 6.8 (q, 1H, CH_2=C$\underline{H}$–), 7.3—8.1 (m, 4H, ArH) ppm.

*Sodium 3-(*p*-Tolylsulfonyl)propionate (**4a**).* The same procedure as that for **2a** was applied to **1b** (4.2 g, 20 mmol) and **2a** (1.5 g, 20 mmol) in 90% ethanol (25 ml) to afford white crystals. Found: C, 48.19; H, 4.22%. Calcd for $C_{10}H_{11}O_2SNa$: C, 47.99; H, 4.43%. IR (KBr) 2960, 2930 (CH_3, CH_2), 1600 ($-COO^-$, Ar), 1280, 1150 (SO_2) cm^{-1}; NMR (D_2O) δ 2.4 (s, 3H, CH_3), 2.7 (t, 2H, CH_2), 3.6 (t, 2H, CH_2), 7.3—7.9 (q, 4H, ArH) ppm.

*3-(*p*-Vinylphenylsulfonyl)propionamide (**3b**).* A solution of **1a** (1.9 g, 10 mmol), **2b** (0.71 g, 10 mmol), and acetic acid (0.6 g, 10 mmol) in 90% ethanol (20 ml) was stirred at room temperature for 12 h. The reaction mixture with a small amount of precipitate was extracted with $CHCl_3$.

The extreact was washed with satd aq $NaHCO_3$, dried over anhyd Na_2SO_4, and evaporated *in vacuo* below 50 °C to leave a solid, which was recrystallized from ethanol to afford light yellow crystals. Found: C, 55.13; H, 5.92; N, 6.13%. Calcd for $C_{11}H_{13}NO_3S$; C, 55.21; H, 5.48; N, 5.85%. IR (KBr) 3420, 3180 (NH_2), 2900 (CH_2), 1690 (C=O), 1600 (Ar), 1300, 1140 (SO_2), 990, 930 (vinyl) cm^{-1}; NMR (DMSO-d_6+$CDCl_3$) δ 2.5 (t, 2H, CH_2), 3.4 (t, 2H, CH_2), 5.5 (d, 1H, C$\underline{H}_2$=CH–), 6.0 (d, 1H, C$\underline{H}_2$=CH–), 6.8 (q, 1H, CH_2=C$\underline{H}$–), 7.3—8.1 (m, 6H, ArH+NH_2) ppm: Mass (*m/e*) 239 (M^+).

*3-(p-Tolysulfonyl)propionamide (**4b**).* The same reaction procedure as that for **3b** was applied to **1b** (20 mmol) and **2b** (20 mmol) in the presence of AcOH (30 mmol). The reaction mixture provided a white precipitate upon cooling, which was analytically pure without further purification. Found: C, 52.94; H, 5.94; N, 6.40%. Calcd for $C_{10}H_{13}NO_3S$: C, 52.90; H, 5.70; N, 6.17%. IR (KBr) 3420, 3180, (NH_2), 2950 (CH_2), 1700 (C=O), 1600 (Ar), 1325, 1305 (SO_2) cm^{-1}; NMR (DMSO-d_6+$CDCl_3$) δ 2.5 (s, 3H, CH_3), 2.5 (t, 2H, CH_2), 3.4 (t, 2H, CH_2), 7.1—8.1 (m, 6H, ArH+NH_2) ppm; Mass (*m/e*) 227 (M^+, 1), 91 (100).

*3-(p-Vinylphenylsulfonyl)propionitrile (**3c**).* The same procedure as that for **3b** was applied to **1a** (10 mmol) and **2c** (10 mmol) in the presence of AcOH (10 mmol). The clear reaction mixture, when subjected to the same purification procedure except for recrystallization from ethanol–ether, provided pale yellow crystals. Found: C, 59.04; H, 4.96; N, 6.16%. Calcd for $C_{11}H_{11}NO_2S$: C, 59.71; H, 4.56; N, 6.33%. IR (KBr) 2990, 2950 (CH_2), 2250 (CN), 1635 (vinyl), 1600 (Ar), 1305, 1140 (SO_2), 1000, 920 (vinyl) cm^{-1}; NMR (DMSO-d_6+$CDCl_3$) δ 2.8 (t, 2H, CH_2), 3.6 (t, 2H, CH_2), 5.5 (d, 1H, C$\underline{H}_2$=CH–), 6.0 (d, 1H, C$\underline{H}_2$=CH–), 6.8 (q, 1H, CH_2=C$\underline{H}$–), 7.4—8.1 (m, 4H, ArH) ppm; Mass (*m/e*) 221 (M^+, 26), 104 (100).

*3-(p-Tolylsulfonyl)propionitrile (**4c**).* The same procedure as that for **3b** was applied to **1b** (20 mmol) and **2c** (20 mmol) in the presence of AcOH (30 mmol). The reaction mixture provided white crystals upon cooling, which were analytically pure without further purification. Found: C. 57.17; H, 5.34; N, 6.69%. Calcd for $C_{10}H_{11}NO_2S$: C, 57.40; H, 5.30; N, 6.69%. IR (KBr) 2990, 2930, 2850 (CH_3, CH_2), 2250 (CN), 1600 (Ar), 1300, 1120, (SO_2) cm^{-1}; NMR (DMSO-d_6+$CDCl_3$) δ 2.5 (s, 3H, CH_3), 2.8 (t, 2H, CH_2), 3.5 (t, 2H, CH_2), 7.3—8.0 (m, 4H, ArH) ppm; Mass (*m/e*) 209 (M^+).

*2-Hydroxyethyl 3-(p-Vinylphenylsulfonyl)propionate (**3d**).* The same procedure as that for **3b** was applied to **1a** (10 mmol) and **2d** (10 mmol) in the presence of AcOH (10 mmol) to afford a viscous liquid, which was purified by silica gel column chromatography using ethanol for elution (a viscous pale yellow liquid). Found: C, 54.20; H, 5.80%. Calcd for $C_{13}H_{16}O_5S$: C, 54.92; H, 5.32%. IR ($CHCl_3$) 3500 (OH), 2940, 2900 (CH_2), 1740 (ester), 1640 (vinyl), 1600 (Ar), 1310, 1140 (SO_2), 980, 920 (vinyl) cm^{-1}; NMR ($CDCl_3$) δ 2.6 (s, 1H, OH), 2.8 (t, 2H, CH_2), 3.3—4.0 (m, 4H, $2CH_2$), 4.2 (t, 2H, CH_2), 5.5 (d, 1H, C$\underline{H}_2$=CH–), 5.9 (d, 1H, C$\underline{H}_2$=CH–), 7.8 (q, 1H, CH_2=C$\underline{H}$–), 7.3—8.0 (m, 4H, ArH) ppm; Mass (*m/e*) 284 (M^+, 1), 254 (100).

*2-Hydroxyethyl 3-(p-Tolylsulfonyl)propionate (**4d**).* The same procedure as that for **3b** was applied to **1b** (20 mmol) and **2d** (20 mmol) in the presence of AcOH (30 mmol) to afford a viscous yellowish green liquid. Found: C, 52.74; H, 5.89%. Calcd for $C_{12}H_{16}O_5S$: C, 52.93; H, 5.92%. IR ($CHCl_3$) 3450 (OH), 2950, 2900 (CH_3, CH_2), 1740 (ester), 1600 (Ar), 1310, 1145 (SO_2) cm^{-1}; NMR ($CDCl_3$) δ 2.5 (s, 3H, CH_3), 2.5 (s, 1H, OH), 2.7 (t, 2H, CH_2), 3.2—4.0 (m, 4H, 2 CH_2), 4.2 (t, 2H, CH_2), 7.2—8.0 (q, 4H, ArH) ppm; Mass (*m/e*) 254 (M^+-H_2O).

References

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