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SHORT COMMUNICATIONS

Enantioselective Addition of β-Oxosulfoxide to ω-Nitrostyrene in the Presence of Nickel Complex

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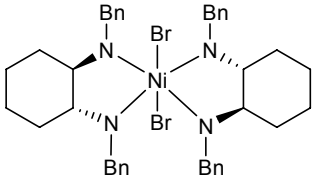
The effective strategy of synthesis of chiral organic compounds is asymmetrical addition of sulfur-containing nucleophiles [1–3] by Michael reaction. The application of organic catalysts to reactions of β-oxosulfones with electron-deficient alkenes allowed an achievement of high enantioselectivity [4–6], but asymmetrical reactions of β-oxosulfoxides as Michaels donors were not investigated till today. The capability of sulfoxides to generate complexes with transition metals [7] makes promising the use of metal complex catalysts in these reactions.

In continuation of the research on the enantioselective addition by Michael reaction [8-10], we have found that the nickel complex (*R*,*R*)-(**I**) (Scheme 1) is an effective catalyst for the reaction of β-oxosulfoxide **II** with ω-nitrostyrene (**III**) (Scheme 2).

Reaction product **IV** was obtained after recrystallisation as an individual diastereomer (according to ^{1}H and ^{13}C NMR data). Further oxidation of sulfoxide **IV** with *m*-chloroperbenzoic acid led to the formation of sulfone **V** (*ee* > 99% according to HPLC).

Basing on the published data on the stereoselectivity of the 1,3-dicarbonyl compounds addition to ω-nitrostyrene in the presence of (*R*,*R*)-(**I**) complex [11] the (*S*)-configuration may be attributed to the stereo center in the position *3* of compounds **IV** and **V**. The data on the $^{3}J_{HH}$ value for the CH groups of (3*S*,4*S*)-5-nitro-4-phenyl-3-(phenylsulfonyl)pentan-2-one [12] which possesses a similar structure suggest the *anti*-configuration of the isolated diastereomer. Hence the (2*S*,3*S*)-configuration may be attributed to compound **IV** and **V**.

Scheme 1.

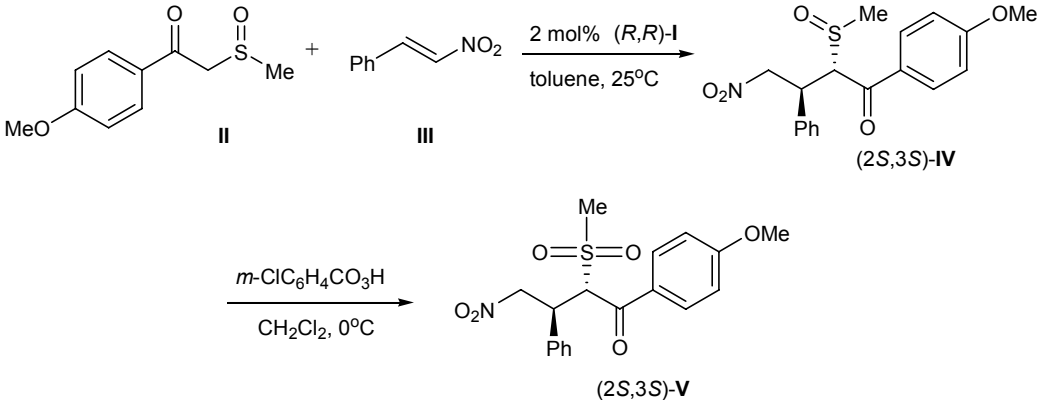


(*R*,*R*)-**I**

(2*S*,3*S*)-(–)-2-(Methylsulfinyl)-1-(4-methoxyphenyl)-4-nitro-3-phenylbutan-1-one (IV). To a solution of 1.17 g (5.52 mmol) of sulfoxide **II** [13] and 0.87 g (5.83 mmol) of ω-nitrostyrene (**III**) in 1.5 mL of toluene was added 89.0 mg (0.11 mmol, 2 mol%) of complex **I** [11] and the mixture was kept for 48 h at 25ºC. The precipitate was filtered off and recrystallized from 15 mL of ethanol. Yield 0.48 g (24%), mp 146–148ºC. $[\alpha]_D^{20}$ –62.5º (*c* 2.5, $CHCl_3$). ^{1}H NMR spectrum, δ, ppm: 2.34 s (3H, CH_3SO), 3.88 s (3H, CH_3O), 4.41–4.45 m (1H, C<u>H</u>Ph), 4.75–4.89 m (3H, CH_2NO_2, CHSO), 6.97 d (2H, OC_6H_4, $^{3}J_{HH}$ 8.9 Hz), 7.30–7.37 m (5H, Ph), 7.95 d (2H, OC_6H_4, $^{3}J_{HH}$ 8.9 Hz). ^{13}C NMR spectrum, δ, ppm: 37.68 (CH_3SO), 42.88 (<u>C</u>HPh), 55.78 (CH_3O), 66.62 (CHSO), 77.83 (CH_2NO_2), 114.59 (C^{3}, O<u>C</u>$_6$H$_4$), 128.40 (C^{2}, Ph), 129.00 (C^{4}, Ph), 129.52 (C^{3}, Ph), 131.32 ($C^{1,2}$, OC_6H_4), 135.63 (C^{1}, Ph) 164.76 (C^{4}, OC_6H_4), 190.85 (C=O). Found, %: C 59.73; H 5.39; N 3.92; S 8.75. $C_{18}H_{19}NO_5S$. Calculated, %: C 59.82; H 5.30; N 3.88; S 8.87.

(2*S*,3*S*)-(–)-2-(Methylsulfonyl)-1-(4-methoxyphenyl)-4-nitro-3-phenylbutan-1-one (V). The solution of 1.08 g (3.00 mmol) of compound **IV** and 1.48 g (6.00 mmol) of 70% *m*-chloroperbenzoic acid in 20 mL of methylene chloride was stirred at 25ºC for 48 h, then washed with saturated solution of sodium hydrogen carbonate, dried with sodium sulfate, and evaporated in a vacuum. The precipitate was washed with diethyl ether, filtered off, and dried. Yield 0.56 g

Scheme 2.



(49%), mp 132–134°C, $[\alpha]_D^{20}$ –58.0° (*c* 2.5, $CHCl_3$). ^1H NMR spectrum, δ, ppm: 2.70 s (3H, CH_3SO_2), 3.86 s (3H, CH_3O), 4.53–4.58 m (1H, C<u>H</u>Ph), 4.94 d.d (1H, CH_2NO_2, $^2J_{HH}$ 13.8, $^3J_{HH}$ 9.4 Hz), 5.06 d.d (1H, CH_2NO_2, $^2J_{HH}$ 13.8, $^3J_{HH}$ 4.1 Hz), 5.35 d (1H, $CHSO_2$, $^3J_{HH}$ 6.6 Hz), 6.92 d (2H, OC_6H_4, $^3J_{HH}$ 9.2 Hz), 7.25–7.35 m (5H, Ph), 7.85 d (2H, OC_6H_4, $^3J_{HH}$ 9.2 Hz). ^{13}C NMR spectrum, δ, ppm: 41.48 (CH_3SO_2), 42.95 (<u>C</u>HPh), 55.81 (CH_3O), 70.19 ($CHSO_2$), 76.83 (CH_2NO_2), 114.54 (C^3, OC_6H_4), 128.31 (C^2, Ph), 129.11 (C^4, Ph), 129.56 (C^3, Ph), 131.78 ($C^{1,2}$, OC_6H_4), 135.35 (C^1, Ph) 165.17 (C^4, OC_6H_4), 190.19 (C=O). Found, %: C 57.20; H 5.14; N 3.79; S 8.36. $C_{18}H_{19}NO_6S$. Calculated, %: C 57.28; H 5.07; N 3.71; S 8.50. HPLC: (2*S*,3*S*)-(–)-(V), t_r 31.0 min; (2*R*,3*R*)-(+)-(V), t_r 39.4 min.

^1H, ^{13}C NMR spectra were registered on a spectrometer Jeol JNM ECX-400 (400 MHz) in $CDCl_3$. Elemental analysis was carried out on a Euro Vector EA-3000 analyzer. The optical rotation angles were measured on an automatic polarimeter Rudolph Research Analytical Autopol V Plus. Enantiomeric composition of compound **V** was determined with the HPLC method on Waters chromatograph (column Chiralpak AD-3, hexane–isopropyl alcohol, 80 : 20, 1.0 mL/min). The signals attribution was carried out by the retention time of the optical antipode (2*R*,3*R*)-(**V**), obtained by the same method as (2S,3*S*)-(**V**) using the (*S*,*S*)-(**I**) complex.

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