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Selective Hydrogenation of Conjugated Unsaturated Ketones Containing a Hydroxyaryl Substituent in the β-Position

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Abstract—A high selectivity was achieved in the Ni_2B-catalyzed hydrogenation of α,β-unsaturated ketones containing a hydroxyaryl (phenolic) substituent in the β-position. The developed hydrogenation procedure was used to synthesize natural compounds of the phenylpropane series and their structural analogs.

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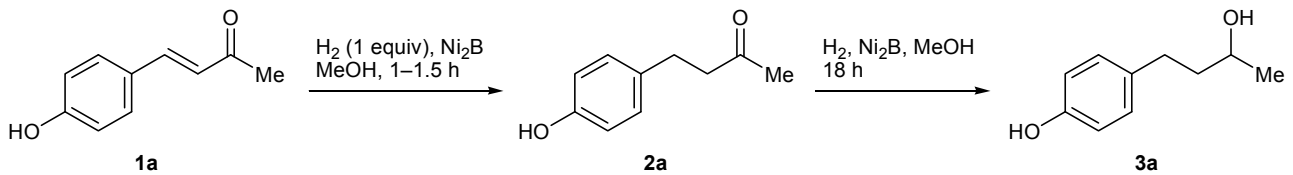
Reduction of α,β-unsaturated carbonyl compounds is widely used in organic synthesis when selective transformation of functional groups is necessary. However, despite a large number of known methods and reagents [1], desired selectivity for some substrates could not always be achieved [2, 3]. We previously reported [3] the synthesis of raspberry ketone (rheosmin) and structurally related zingerone by hydrogenation of α,β-unsaturated precursors in the presence of a cheap catalyst (nickel boride Ni_2B). The selectivity for 1,4-reduction exceeded 98%. The proposed procedure can be used to obtain other compounds of the phenylpropane series. In this article we describe hydrogenation of accessible aldolization/crotonization products with the formation of a number of rheosmin and zingerone analogs. The effect of the substituent nature on the selectivity and rate of the reduction of α,β-unsaturated ketones was also studied.

An interesting peculiarity of the hydrogenation of enones containing a hydroxyaryl substituent in the β-position is discoloration of the reaction mixture when the initial unsaturated ketone is consumed completely (disappearance of conjugated bond system), so that it is easy to detect the end of the reaction and attain selective reduction of the double bond. According to our data, hydrogenation over a longer time involves the carbonyl group up to its complete reduction (Scheme 1). As a result, 4-hydroxybenzylideneacetone (**1a**) under the same conditions can be converted to 1,4-reduction product **2a** (rheosmin) or the corresponding alcohol **3a** (rhododendrol).

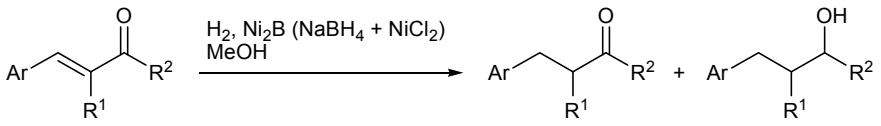
The hydrogenation of structurally related compounds **1b**–**1g** (Scheme 2) was carried out under similar conditions, and the reaction completion was determined by discoloration of the reaction mixture. The corresponding saturated ketones **2b**–**2g** were isolated in no less than 65% yield. The selectivity for 1,4-reduction was evaluated by the molar ratio of saturated ketone **2** and saturated alcohol **3** in the reaction mixture according to the GLC data. The selectivity in the hydrogenation of zingerone (**2b**) was comparable with that in the reduction of rheosmin (**2a**, 98%). The hydrogenation of salicylideneacetone **1c** was characterized by a lower selectivity (93%). The substituent on the double bond in the α-position (enone **1d**), as well as *tert*-butyl substituent on the carbonyl carbon atom (enones **1e**, **1f**), appreciably reduced the hydrogenation rate, the selectivity being 96–97%. The hydrogenation of camphor derivative **1g** was the most difficult to accomplish. In this case, increased load of

Scheme 1.

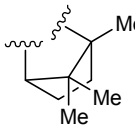


1a **2a** **3a**

Scheme 2.



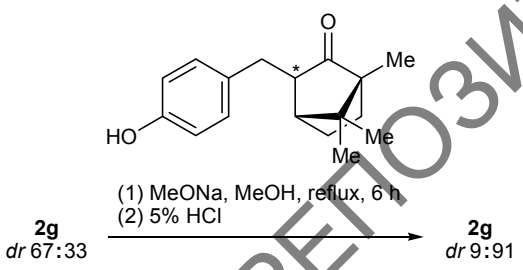
Ar = 3-MeO-4-HOC$_6$H$_3$, R^1 = H, R^2 = Me (**b**); Ar = 2-HOC$_6$H$_4$, R^1 = H, R^2 = Me (**c**); Ar = 4-HOC$_6$H$_4$, R^1 = R^2 = Me (**d**);

Ar = 4-HOC$_6$H$_4$, R^1 = H, R^2 = *t*-Bu (**e**); Ar = 3-MeO-4-HOC$_6$H$_3$, R^1 = H, R^2 = *t*-Bu (**f**); Ar = 4-HOC$_6$H$_4$, R^{1}R^2 =  (**g**).

the catalyst, longer reaction time, and higher temperature were necessary, but no side reduction of the carbonyl group occurred.

Saturated ketone **2g** was isolated as a mixture of diastereoisomers at a ratio of 2:1. Base-catalyzed epimerization of **2g** changed the diastereoisomer ratio in the opposite direction (Scheme 3), presumably in favor of the *trans* isomer (9:91). The epimer ratio was determined from the intensities of signals from one benzylic proton in the ^{1}H NMR spectra, which were observed as doublets of doublets at δ 3.16 and 3.09 ppm. The stereoisomer ratio no longer changed after double recrystallization of the isomer mixture.

Scheme 3.



Initial unsaturated ketones **1a**–**1g** are readily available by condensation of aromatic aldehydes with the corresponding ketones (see Experimental). Unexpected difference in the reactivities of 4-hydroxybenzaldehyde and vanillin toward pinacolone was observed in the synthesis of enones **1e** and **1f**, respectively. In the first case, the reaction smoothly afforded the target product on heating in methanol in the presence of sodium methoxide with almost complete conversion of the reactants, and there was no need of introducing protecting groups. Vanillin failed to react with pinacolone under analogous conditions, and only the initial compounds were detected in the reaction mixture. The low reactivity of vanillin may be related to the formation of poorly soluble sodium phenoxide, as was noted previously [4]. By replacing sodium methoxide by potassium methoxide we obtained the corresponding potassium phenoxide which is readily soluble in methanol; however, this in no way favored the reaction. The condensation was successful only with vanillin protected by a tetrahydropyranyl group. The observed strong effect of the *meta* substituent on the condensation may be rationalized by coordination of the methoxy group to metal ion, which additionally stabilizes phenoxide ion and hence reduces the reactivity of the aldehyde carbonyl group.

In summary, we have proposed a simple procedure for selective 1,4-reduction of unsaturated ketones containing a hydroxyaryl substituent in the β-position. A number of structurally related phenylpropane derivatives, including natural raspberry ketone and zingerone, have been synthesized via aldolization/crotonization of aromatic aldehydes with ketones and subsequent hydrogenation in the presence of nickel boride.

EXPERIMENTAL

The ^{1}H and ^{13}C NMR spectra were recorded from solutions in $CDCl_3$ on a Bruker Avance 500 spectrometer at 500 and 125 MHz, respectively. The IR spectra were measured on a Bruker Vertex 70 spectrometer. The melting points were determined in capillaries. Gas chromatographic–mass spectrometric analyses were obtained on a Shimadzu GCMS-QP2010 instrument using an Equity-5 capillary column. Silica gel (70–230 mesh) was used for column chromatography; TLC was performed on Silufol plates using hexane–ethyl acetate as eluent; spots were detected by treatment with a 10% alcoholic solution of phosphomolybdic acid. The elemental analyses were obtained with a Thermo Scientific Flash 2000 CHNS/O analyzer. The solvents were dried by standard methods and distilled prior to use.

(3*E*)-4-(4-Hydroxyphenyl)but-3-en-2-one (**1a**) was synthesized as described in [5] and was purified by recrystallization from toluene–ethyl acetate (2:1).

(3*E*)-4-(4-Hydroxy-3-methoxyphenyl)but-3-en-2-one (**1b**) was synthesized according to [5] and was purified by recrystallization from 75% isopropyl alcohol.

(3*E*)-4-(2-Hydroxyphenyl)but-3-en-2-one (**1c**) was prepared by condensation of salicylaldehyde with acetone according to the same procedure as that used for the synthesis of **1a** and **1b** [5], but the reaction time was shortened to 6 h. The product was purified by recrystallization from benzene with addition of charcoal [6].

(3*E*)-4-(4-Hydroxyphenyl)-3-methylbut-3-en-2-one (**1d**) was synthesized according to the procedure reported in [7].

(1*E*)-1-(4-Hydroxyphenyl)-4,4-dimethylpent-1-en-3-one (1e). 4-Hydroxybenzaldehyde, 5.0 g (40.9 mmol), and pinacolone, 9.0 g (90 mmol), were added to a solution of 100 mmol of sodium methoxide in 45 mL of methanol. The mixture was refluxed for 9 h and concentrated under reduced pressure. The residue was treated with 100 mL of 10% aqueous HCl and extracted with ethyl acetate (4×25 mL). The combined extracts were vigorously shaken for 30 min with a solution prepared from 20 g of sodium sulfite, 100 mL of water, and 3.9 g of 96% sulfuric acid, washed with water (10 mL) and saturated solutions of $NaHCO_3$ and NaCl (10 mL each), and dried over Na_2SO_4. The solvent was distilled off under reduced pressure, and the residue was recrystallized from toluene. Yield 6.35 g (76%), light yellow crystals, mp 125–128°C. IR spectrum (KBr), ν, cm^{-1}: 3150 (OH), 1665 (C=O), 1600 (C=C). ^{1}H NMR spectrum, δ, ppm: 1.22 s (9H, *t*-Bu), 6.92–6.93 m (2H, H_{arom}), 7.03 d (1H, CH=, *J* = 15.5 Hz), 7.46–7.47 m (2H, H_{arom}), 7.67 d (1H, CH=, *J* = 15.5 Hz), 7.83 br.s (1H, OH). ^{13}C NMR spectrum, δ_C, ppm: 26.4 (3C, CH_3), 43.2, 116.0 (2C, CH), 117.7 (CH), 126.9, 130.4 (2C, CH), 144.0 (CH), 158.7, 206.3 (C=O). Found, %: C 76.60; H 7.84. $C_{13}H_{16}O_2$. Calculated, %: C 76.44; H 7.90.

(1*E*)-1-(4-Hydroxy-3-methoxyphenyl)-4,4-dimethylpent-1-en-3-one (1f). A solution of 2.5 g (16.4 mmol) of vanillin, 2.1 g (25.0 mmol) of dihydropyran, and 0.1 g (0.4 mmol) of pyridinium *p*-toluenesulfonate in 10 mL of anhydrous methylene chloride was stirred for 40 h at room temperature. When the reaction was complete, the mixture was washed with a saturated solution of sodium hydrogen carbonate and dried over Na_2SO_4, and the solvent was distilled off under reduced pressure. The residue was dissolved in 15 mL of methanol containing 20 mmol of sodium methoxide, 2.5 g (25 mmol) of pinacolone was added, and the mixture was stirred for 20 h at room temperature and concentrated under reduced pressure. The residue was treated with 20 mL of water and 20 mL of ethyl acetate, the organic layer was separated, and the aqueous layer was extracted with ethyl acetate (2×10 mL). The extracts were combined with the organic phase, washed with water (10 mL) and saturated solutions of $NaHCO_3$ and NaCl (10 mL each), and dried over Na_2SO_4. The solvent was distilled off under reduced pressure, the crude condensation product was dissolved in 20 mL of methanol, 0.06 g (0.24 mmol) of pyridinium *p*-toluenesulfonate was added, and the mixture was kept for 3 h at room temperature. Triethylamine, 0.1 mL, was added, the solvent was distilled off under reduced pressure, the residue was treated with 10 mL of water and 10 mL of ethyl acetate, the organic phase was separated, and the aqueous phase was extracted with ethyl acetate (2×5 mL). The combined extracts were vigorously shaken for 10 min with a solution prepared from 4 g of Na_2SO_3, 20 mL of water, and 0.8 g of 96% H_2SO_4, washed with water (5 mL) and saturated solutions of $NaHCO_3$ and NaCl (5 mL each), and dried over Na_2SO_4. The solvent was distilled off under reduced pressure to obtain 3.5 g of the crude product with a purity of >90% (according to the ^{1}H NMR data), which was purified by silica gel column chromatography (hexane–ethyl acetate, 5:1). Yield 3.35 g (87%), oily material. IR spectrum (KBr), ν, cm^{-1}: 3200 (OH), 1645 (C=O), 1590 (C=C). ^{1}H NMR spectrum, δ, ppm: 1.22 s (9H, *t*-Bu), 3.92 s (3H, CH_3O), 6.11 br.s (1H, OH), 6.90–6.91 m (1H, H_{arom}), 6.97 d (1H, CH=, *J* = 15.5 Hz), 7.02–7.03 m (1H, H_{arom}), 7.13–7.14 m (1H, H_{arom}), 7.62 d (1H, CH=, *J* = 15.5 Hz). ^{13}C NMR spectrum, δ_C, ppm: 26.4 (3C, CH_3), 43.1, 55.9 (CH_3), 110.2 (CH), 114.8 (CH), 118.2 (CH), 122.8 (CH), 127.4, 143.2 (CH), 146.7, 147.9, 204.3 (C=O). Found, %: C 71.50; H 7.70. $C_{14}H_{18}O_3$. Calculated, %: C 71.77; H 7.74.

(3*E*)-3-(4-Hydroxybenzylidene)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-one (1g) was synthesized according to modified procedure [8]. A solution of 2.0 g (16.4 mmol) of 4-hydroxybenzaldehyde, 2.1 g (25.0 mmol) of dihydropyran, and 0.1 g (0.4 mmol) of pyridinium *p*-toluenesulfonate in 10 mL of anhydrous methylene chloride was stirred for 20 h at room temperature. When the reaction was complete, the mixture was washed with a saturated solution of sodium hydro-

gen carbonate and dried over Na_2SO_4, and the solvent was distilled off under reduced pressure. The residue was dissolved in 10 mL of DMSO, 2.0 g (35.7 mmol) of powdered potassium hydroxide, 2.20 g (14.5 mmol) of (±)-camphor were added, and the mixture was stirred for 20 h at room temperature, diluted with 100 mL of water, and extracted with ethyl acetate (3×20 mL). The combined extracts were washed with water (20 mL) and saturated solutions of $NaHCO_3$ and NaCl (20 mL each) and dried over Na_2SO_4, and the solvent was distilled off under reduced pressure. The tetrahydropyranyl protecting group was removed as described above in the synthesis of **1f**. The crude product was purified by crystallization from methanol. Yield 2.38 g (64%), colorless crystals, mp 207–212°C. IR spectrum (KBr), ν, cm^{-1}: 3230 (OH), 1660 (C=O), 1592 (C=C). ^{1}H NMR spectrum, δ, ppm: 0.81 s (3H, CH_3), 1.00 s (3H, CH_3), 1.03 s (3H, CH_3), 1.48–1.60 m (2H), 1.75–1.81 m (1H), 2.13–2.20 m (1H), 3.08 br.d (1H, **H**CC=CH, J = 4.1 Hz), 5.65 br.s (1H, OH), 6.86–6.89 m (2H, H_{arom}), 7.19 br.s (1H, C=CH) 7.38–7.41 m (2H, H_{arom}).

Hydrogenation of unsaturated ketones 1a–1g (*general procedure*). Sodium tetrahydridoborate, 0.46 g (12.1 mmol), was added in portions with stirring to a solution of 1.10 g (4.63 mmol) of $NiCl_2 \cdot 6H_2O$ in 20 mL of methanol, cooled to 0°C. The resulting suspension was stirred for 15 min at 0°C and refluxed for 20 min under argon. The mixture was then cooled to room temperature, 9.25 mmol of ketone **1a**–**1g** was added, and the miixture was stirred in a hydrogen atmosphere. When the green color of the reaction mixture disappeared, hydrogen supply was turned off, and the mixture was filtered. The precipitate of nickel boride was additionally washed with a small amount of methanol, and the filtrate was evaporated under reduced pressure. The residue was dissolved in ethyl acetate (20 mL), the solution was washed with a saturated aqueous solution of ammonium chloride (20 mL), the organic phase was separated, and the aqueous phase was extracted with ethyl acetate (10 mL). The combined organic phases were washed with saturated solutions of $NaHCO_3$ and NaCl (10 mL each), dried over Na_2SO_4, and evaporated under reduced pressure. The residue was purified by crystallization from appropriate solvent mixture or by column chromatography.

4-(4-Hydroxyphenyl)butan-2-one (2a) was obtained by hydrogenation of 1.5 g (9.25 mmol) of enone **1a** at 25°C (reaction time 1 h). The product was purified by crystallization from methanol–water (1:3). Yield 1.14 g (75%), colorless crystals, mp 82–83°C. The spectral parameters of **2a** were consistent with those given in [5].

1-(4-Hydroxyphenyl)propan-2-ol (3a) was obtained in a similar way from 1.5 g (9.25 mmol) of enone **1a**; after disappearance of green color, the hydrogenation was continued for 18 h. The product was purified by crystallization from methanol–water (1:2). Yield 1.0 g (65%), colorless crystals, mp 70–73°C. The spectral parameters of **3a** were consistent with those given in [9].

4-(4-Hydroxy-3-methoxyphenyl)butan-2-on (2b) was obtained from 1.78 g (9.26 mmol) of enone **1b** at 25°C (reaction time 1.5 h). The product was purified by silica gel column chromatography using petroleum ether–ethyl acetate (1:5 to 1:3) as eluent. Yield 1.69 g (94%), viscous liquid which crystallized on storage in a refrigerator, mp 39–40°C. Alternatively, the crude product was recrystallized from methanol–water (1:3) using a few crystals of pure compound **2b** to initiate crystallization. Yield 1.22 g (68%), colorless crystals, mp 41–42°C. The spectral parameters of the product were consistent with those given in [5].

4-(2-Hydroxyphenyl)butan-2-one (2c) was obtained from 1.5 g (9.25 mmol) of enone **1c** at 25°C (reaction time 1 h). The product was purified by silica gel column chromatography using petroleum ether–ethyl acetate (1:10 to 1:5) as eluent. Yield 1.33 g (88%), viscous liquid which crystallized on storage in a refrigerator, mp 38–40°C. The spectral parameters of the product were consistent with those given in [10].

4-(4-Hydroxyphenyl)-3-methylbutan-2-one (2d) was obtained from 1.63 g (9.25 mmol) of enone **1d** at 25°C (reaction time 3 h). The product was purified by silica gel column chromatography using petroleum ether–ethyl acetate (1:10 to 1:3) as eluent. Yield 1.5 g (91%), viscous liquid. The spectral parameters of the product were consistent with those given in [11].

1-(4-Hydroxyphenyl)-4,4-dimethylpentan-3-one (2e) was obtained from 1.89 g (9.25 mmol) of enone **1e** at 35–40°C (reaction time 3 h). The product was purified by crystallization from methanol–water (4:3). Yield 1.36 g (71%), colorless crystals, mp 84–86.5°C. IR spectrum (KBr), ν, cm^{-1}: 3050 (OH), 1700 (C=O). ^{1}H NMR spectrum, δ, ppm: 1.11 s (9H, *t*-Bu), 2.76–2.83 m (4H, CH_2CH_2), 6.36 br.s (1H, OH), 6.77–6.79 m (2H, H_{arom}), 7.02–7.04 m (2H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 26.2 (3C, CH_3), 29.2 (CH_2), 38.8 (CH_2), 44.1, 115.3 (2C, CH), 129.4 (2C, CH), 133.1,

154.1, 216.6 (C=O). Found, %: C 75.50; H 8.75. $C_{13}H_{18}O_2$. Calculated, %: C 75.69; H 8.80.

1-(4-Hydroxy-3-methoxyphenyl)-4,4-dimethylpentan-3-one (2f) was obtained from 2.17 g (9.26 mmol) of enone **1f** at 35–40°C (reaction time 4 h). The product was purified by silica gel column chromatography using petroleum ether–ethyl acetate (1:15 to 1:10) as eluent. Yield 1.99 g (91%), viscous liquid which crystallized on storage in a refrigerator, mp 60–65°C. An analytical sample was obtained by recrystallization from methanol–water (4:3), mp 66–68.5°C. IR spectrum (KBr), ν, cm^{-1}: 3062 (OH), 1701 (C=O). ^{1}H NMR spectrum, δ, ppm: 1.10 s (9H, *t*-Bu), 2.74–2.82 m (4H, CH_2CH_2), 3.86 s (3H, CH_3O), 5.56 br.s (1H, OH), 6.64–6.69 m (2H, H_{arom}), 6.81–6.82 m (1H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 26.2 (3C, CH_3), 29.7 (CH_2), 38.7 (CH_2), 44.0, 55.8 (OCH_3), 111.1 (CH), 114.2 (CH), 120.7 (CH), 133.4, 143.8, 146.3, 215.1 (C=O). Found, %: C 71.04; H 8.50. $C_{14}H_{20}O_3$. Calculated, %: C 71.16; H 8.53.

3-(4-Hydroxybenzyl)-1,7,7-trimethylbicyclo-[2.2.1]heptan-2-one (2g) was obtained from 2.37 g (9.24 mmol) of enone **1g** in methanol–tetrahydrofuran (1:1) using a double amount of nickel boride; the mixture was stirred for 5 h at 50°C in a hydrogen atmosphere. The crude product (a mixture of diastereoisomers at a ratio of 2:1) was dissolved in 30 mL of methanol containing 30 mmol of sodium methoxide. The mixture was refluxed for 6 h, the solvent was removed under reduced pressure, and the residue was treated with 40 mL of 5% aqueous HCl and extracted with ethyl acetate (3×15 mL). The combined extracts were washed with water (10 mL) and saturated aqueous solutions of $NaHCO_3$ and NaCl (10 mL each) and dried over Na_2SO_4. The solvent was removed under reduced pressure, and the residue was recrystallized twice from toluene. Yield 1.82 g (76%), colorless crystals, mp 129–132°C. IR spectrum (KBr), ν, cm^{-1}: 3245 (OH), 1738 (C=O). ^{1}H NMR spectrum (a mixture of diastereoisomers at a ratio of 9:91; signals of the major stereoisomer are given), δ, ppm: 0.85 s (3H, CH_3), 0.93 s (3H, CH_3), 0.97 s (3H, CH_3), 1.33–1.38 m (1H), 1.69–1.80 m (3H), 1.93–1.95 m (1H), 2.44 d.d (1H, $C_6H_4C\mathbf{H}_2$, J = 14.4, 11.1 Hz), 2.65–2.69 m [1H, C(O)CH], 3.09 d.d (1H, $C_6H_4C\mathbf{H}_2$, J = 14.4, 4.5 Hz), 5.82 br.s (1H, OH), 6.77–6.80 m (2H, H_{arom}), 7.03–7.05 m (2H, H_{arom}). ^{13}C NMR spectrum (signals of the major isomer are given), δ_C, ppm: 9.51 (CH_3), 19.21 (CH_3), 19.47 (CH_3), 20.19 (CH_2), 30.93 (CH_2), 31.76 (CH_2), 45.68 (CH), 45.73, 52.06 (CH), 58.96, 115.35 (2C, CH), 129.46 (2C, CH), 131.84, 154.16, 221.91 (C=O). Found, %: C 79.40; H 8.70. $C_{17}H_{22}O_2$. Calculated, %: C 79.03; H 8.58.

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