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ULTRASONIC ACCELERATED HYDROGENATION OF α,β-UNSATURATED KETONES WITH RANEY NICKEL CATALYST

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Abstract: Various α,β -unsaturated ketones and coumarin were hydrogenated in high yields with ultrasonic activated Raney Nickel. Only C=C bonds were reduced. In the presence of ultrasonic waves, the catalyst is reusable.

Application of ultrasound (US) in promoting metal-catalyzed organic reactions have been intensely investigated recently¹⁻¹². Maltsev² reported that ultrasonic irradiation can considerably enhance the reactivity of some metal catalysts such as Pt, Pd and Rh. Boudjouk and Han⁸ found that hydrogenation of various olefins could be performed in high yields with the formic acid as hydrogen supplier and palladium-on-carbon as catalyst in the presence of ultrasonic waves. Suslick *et al*¹⁰ discovered that irradiation of high-intensity

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ultrasound could increased the hydrogenation activity of nickel powder by over 10^5 . Ultrasonic activated nickel powder was proved to be an effective catalyst in the hydrogenation of olefins. Recently, we¹¹ have reported that nitroarenes can be reduced to the corresponding aminoarenes in excellent yields with ultrasonic-activated nickel powder and hydrazine hydrate in the presence of ultrasonic waves. We also obtained various sulfones by ultrasonic-assisted coupling reactions of arenesulfonyl chlorides with alkyl halides¹². Here we hope to report the ultrasonic-accelerated hydrogenation of α , β -unsaturated ketones and coumarin with Raney Nickel as catalyst.

There has been considerable interest in the selective reduction of α,β unsaturated carbonyl compounds¹³. PtO₂ or Pd/C were normally used as catalysts¹⁴. We found that various α,β -unsaturated ketones and coumarin could be hydrogenated at room temperature and ambient hydrogen pressure in the presence of ultrasonic-irradiated Raney nickel. Only carbon-carbon double bonds were reduced (Scheme 1 and 2). The yields are excellent and the reactions were completed within 30 mins (Table 1). In contrast, hydrogenation of the same substrates with normal Raney nickel without ultrasonic irradiation proceeded very slowly and the yields are poor.

Scheme 1

Ar¹CH=CHCOAr² +H₂ $\xrightarrow{\text{Raney Ni, US, r.t.}}$ Ar¹CH₂CH₂COAr² 1a-e 2a-e

	Ar ¹	Ar ²		Ar ¹	Ar ²
2a	C ₆ H ₅	C ₆ H ₅	2d	p-CH ₃ OC ₆ H ₄	C ₆ H ₅
2b	C ₆ H ₅	p-CH ₃ C ₆ H ₄	2e	3,4-(CH ₂ O ₂)C ₆ H ₃	C ₆ H₅
2c	$p-ClC_6H_4$	C ₆ H ₅			



Table 1.	Hydrog	genation	of α,β·	unsaturated	l ketones	and c	coumarin
 		and the second se			·····		

Products	with US		without US			
	Reaction	Yield	Reaction	Yield		
	Time(min)	(%)	Time (min)	(%)		
2a	25	95	50	11		
2b	30	96	80	39		
2c	30	85	60	54		
2d	20	78	60	63		
2e	15	89	60	80		
2f	50	100	120	57		

It was found that the Raney Nickel catalyst could be reused if ultrasonic irradiation was applied. For the hydrogenation of compound 1,3-Diphenyl-2-propen-1-one (1a), the Raney nickel catalyst could be cycled up to 4 times without substantial decreasing of the reactivity (Table 2). Without the activation of ultrasonic wave, however, the reactivity of the recovered catalyst decreased distinctively. This is in accordance with the observation of Suslick *et al*¹⁰.

with recovered Raney Nickel catalyst*								
Entry	cycle	with US irradiated		without USirradiated				
	S							
		Reaction time	Yield	Reaction time	Yield			
		(min)	(%)	(min)	(%)			
1	1	20	87	20	88			
2	2	40	91	50	95			
3	3	50	91	75	62			
4	4	60	89	60	56			

Table 2. Hydrogenation of 1,3-diphenyl-2-propen-1-one (1a) with recovered Raney Nickel catalyst*

*: All reactions were run at r.t except entry 4 which was done at 50 °C.

As the present method for the selective reduction of α,β -unsaturated ketones and coumarin is simple and easy to handle, it provides a useful alternative way for the preparation of the target compounds.

EXPERIMENTAL

IR spectra were taken on a IDP-440 spectrometer.¹HNMR were taken on a Jeol PMX-60SI spectrometer and chemical shifts (δ) were referred to TMS. Ultrasonic were generated by a KQ-50 Ultrasonic Cleaner. W-2 Raney Nickel was prepared according to literature¹⁵. Melting points were uncorrected.

Reduction of α , β -unsaturated ketone (1a-1e), general procedure:

A suspension of α,β -unsaturated ketone or coumarin (5.0 mmol) and Raney Nickel catalyst (0.21g,wet) in fresh distilled ethyl acetate (25mL) was irradiated by ultrasonic at room temperature under hydrogen atomosphere. When the reaction was completed (TLC monitoring), the mixture was filtered and wsahed with ethyl acetate. The volatiles were removed under vacuum. The crude product obtained was purified by column chromatography on silica gel (300-400 mesh, eluent: ethyl acetate:petroleum (Bp:60-90°C) = 1:20 (V/V)). The results were summarized in Table 1.

Hydrogenation of 1,3-Diphenyl-2-propanen-1-one with recovered Raney Nickel catalyst:

A solution of 1,3-Diphenyl-2-propanen-1-one (4.16g, 20mmol) and the recovered Raney Nickel (0.82g) in fresh distilled ethyl acetate (80mL) was stirred under 0.5-1.0MPa hydrogen pressure at room temperature. Work-up was done as above. The results were summarized in Table 2.

<u>1,3-Diphenyl-1-propanone 2a:</u> Mp: 70-72°C (lit:72-73°C). IR (KBr,cm⁻¹): 1680, 1600, 1580, 1490, 1450. ¹H-NMR (CDCl₃, δppm): 2.83-3.40 (m,4H,-CH₂CH₂-), 6.93-7.93 (m,10H,ArH).

<u>**1-(4-Methylphenyl)-3-phenyl-1-propanone 2b:**</u> Mp: 72-73°C (lit¹⁶:69°C). IR (KBr, cm⁻¹): 1670, 1600, 1490, 1450. ¹H-NMR (CDCl₃, δppm): 2.40 (s, 3H, CH₃), 2.93-3.37 (m, 4H, -CH₂CH₂-), 7.40-7.93 (m, 9H, ArH).

<u>3-(4-Chlorophenyl)-1-phenyl-1-propanone 2c:</u> Mp: 58-59°C (lit¹⁷:56.5-58°C). IR (KBr,cm⁻¹): 1670, 1600, 1580, 1490, 1450. ¹H-NMR (CDCl₃,δppm): 2.87-3.33 (m, 4H, -CH₂CH₂-), 7.13-7.97 (m,9H,ArH).

<u>3-(4-Methoxyphenyl)-1-phenyl-1-propanone 2d:</u> Mp: 69-70°C (lit:68°C). IR (KBr, cm⁻¹): 1680, 1610, 1590, 1500, 1440, 1230, 1030. ¹H-NMR (CDCl₃,δppm): 2.83-3.40 (m,4H,-CH₂CH₂-), 3.73 (s,3H, CH₃O), 6.67-7.97 (m,9H,ArH).

<u>3-(3,4 -Methylenedioxyphenyl) -1-phenyl-1-propanone 2e:</u> Mp: 48-49°C. IR (KBr, cm⁻¹):1680, 1600, 1580, 1480, 1440, 1240, 1030. ¹H-NMR (CDCl₃,δppm): 2.73-3.34 (m, 4H, -CH₂CH₂-), 5.82 (s, 2H,CH₂O₂), 6.64-7.97 (m,8H,ArH).

<u>3,4-Dihydro-2H-1-benzopyran-2-one 2f</u>: Oil (lit: liquid or crystal, Mp: 25 °C). IR (KBr, cm⁻¹): 1610, 1580, 1480, 1450, 1220, 1030. ¹H-NMR (CDCl₃,δppm): 2.60-3.16 (m, 4H, -CH₂CH₂-), 6.83-7.40 (m,4H,ArH).

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