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Research Article

Hydrogen Transfer Reaction of Ketones Under Ru-NHC Catalyst

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Abstract – The reduction of organic compounds is one of the important synthetic processes both in the laboratory and industrially. Transfer hydrogenation, which is practically carried out with metal catalysis, is an important reaction in this respect. Since hydrogen donor molecules are used instead of gaseous hydrogen in the reduction of multiple bonds, it is economical, mild and environmentally friendly. [1] Hydrogen donors such as molecular hydrogen, alcohol, formic acid are catalytically activated by suitable metals or metal complexes. It is known that many Ru, Rh and Ir compounds reduce different substrates in both homogeneous and heterogeneous phases. [2,3] In this study, 5,6-dimethylbenzimidazol-2-ylidene salts, which were synthesized and whose structures were elucidated by spectroscopic methods, were converted into ruthenium-carbene complexes in the reaction medium and their catalytic activation in the transfer hydrogenation reaction of acetophenone derivatives was investigated. When the results were examined, it was seen that this catalyst system was active.

Keywords – Transfer Hydrogenation, Ru-NHC, 5,6-Dimethylbenzimidazole-2-Yliden, Ketone, Alcohol.

I. INTRODUCTION

Catalysts, which increase the rate of a reaction by reducing the activation energy, are the most important element in modern organic synthesis. Because an effective and selective catalyst; reduces operating costs by keeping raw material resources, toxic reagents (solvents), by-products and toxic products to a minimum. Increasing environmental awareness and limited raw material resources have increased the importance of catalysts by causing a shift towards green technology. Catalysts have played a very important role in the economic success achieved by the chemical industry in recent years. For this purpose, effective, new, selective, environmentally friendly catalysts and catalytic systems are needed. *N*-heterocyclic carbenes are ligands widely used in transition metal compounds. The first NHC complexes were described by Öfele [4] and Wanzlick [5] in 1968. However, with the isolation of free imidazole-2-ylidene carbene by Arduengo and his colleagues in 1991, studies on this subject have increased rapidly. Metal-NHC complexes are more stable, odorless and show much more activity in many chemical reactions than their analogs, metal phosphine complexes.

Transfer hydrogenation is the addition of hydrogen to a molecule from a source other than gaseous hydrogen. Transfer hydrogenation can be easily applied in industry and organic synthesis. Because gaseous hydrogen has storage and usage difficulties. In this field of organic synthesis, hydrogen-transfer catalysts based on ruthenium and rhodium diamine and phosphine complexes have been developed. These catalysts

have been used in the reduction of ketones and imines to alcohols and amines. Generally, 2-propanol, which is non-toxic, environmentally friendly and cheap, is used as a hydrogen donor.

For this purpose, *N*-heterocyclic carbene precursors that are stable, effective and functional under catalytic reaction conditions were synthesized, NHC complexes were prepared by interacting with Ru compounds, and their catalytic properties in the hydrogen transfer reaction of ketones was investigated.

II. MATERIALS AND METHOD

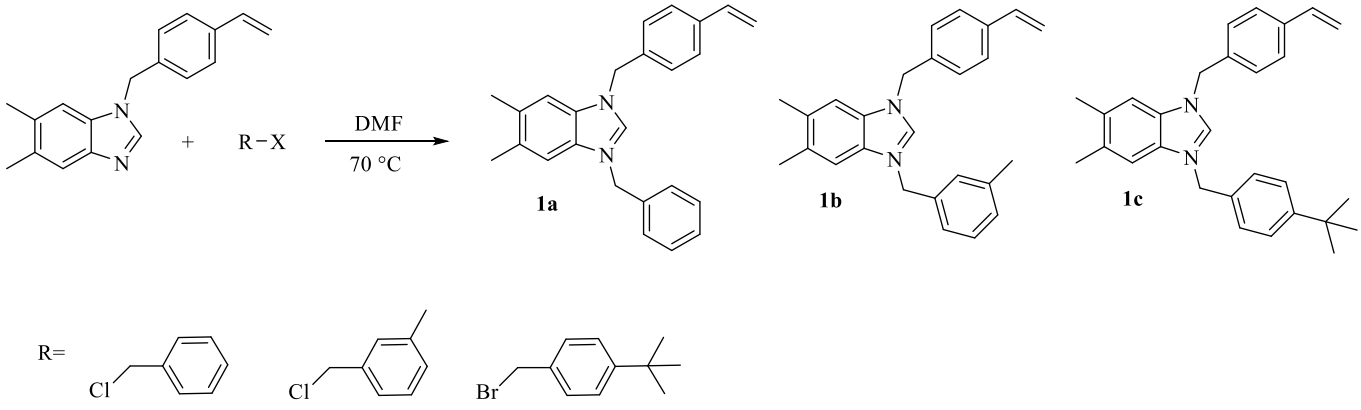
Method

Due to the sensitivity of the synthesized compounds to moisture and oxygen in the air, all experiments were conducted under an inert atmosphere. Before use, glassware was heated under vacuum to remove air and moisture, then filled with inert gas to create an inert atmosphere. Reagents were dried and purified in an inert environment according to methods described in the literature before use. Reagents were dried and purified in an inert environment according to methods described in the literature before use All chemicals and solvents were purchased/acquired from Sigma−Aldrich and Merck. NMR spectra were recorded on a Bruker Ultra Shield 300 MHz NMR. All catalytic reactions were analyzed on a Shimadzu GC2010 Plus system.

III. RESULTS AND DISCUSSIONS

Synthesis of 1-(4-vinylbenzyl)-benzimidazole

Sodium hydride (0.46 g, 20 mmol) was placed in a Schlenk flask, which had been heated under vacuum to remove air and moisture, and washed with hexane. THF (30 mL) was added. 5,6-dimethylbenzimidazole (2.36 g, 20 mmol) was slowly added to the solution, which was stirred at room temperature, and gas evolution was observed. After the complete addition of benzimidazole, the mixture was stirred at room temperature for half an hour, and then 4-vinyl benzyl chloride (3.05 g, 21 mmol) was added. The mixture was stirred overnight at room temperature and then refluxed for five hours in a water bath. THF was removed under vacuum, dichloromethane (20 mL) was added, and the mixture was filtered. The product was crystallized from dichloromethane/diethyl ether. Yield: 88% (2.82 g).



Scheme 1. Synthesis of benzimidazole-2-yliden

1-(4-Vinylbenzyl)-3-(benzyl)-5,6-dimethylbenzimidazolium chloride, 1a

1-(4-Vinylbenzyl)-5,6-dimethylbenzimidazole was dissolved in 10 mL of DMF in a Schlenk flask. Then, benzyl chloride was slowly added. The mixture was stirred at room temperature for one hour and then heated to 70°C for 12 hours. After cooling to room temperature, ether was added to precipitate the solid. The obtained solid was left to crystallize in an ethanol/ether mixture. The resulting solid was washed with ether and dried under vacuum. Yield: 78%. mp: 218-219°C. FT-IR ν(CN) : 1560 cm^{-1} ; 1 H NMR (399.9

MHz, DMSO-d^6 , 25°C): δ = 2.35 (6H, s, 5,6-$(CH_3)_2$-C_6H_2), 5.29 (^{1}H, d, J = 10.8 Hz, $NCH_2C_6H_4CH=CH_2$-4), 5.75 (4H, brs, $NCH_2C_6H_5$ and $NCH_2C_6H_4CH=CH_2$-4), 5.89 (1H, d, J = 10.8 Hz, NCH $_2C_6$ H_4 CH═CH_2-4), 6.73 (1H, dd, J = 12.3 and 10.8 Hz, NCH $2C_6$ H_4 CH=CH $_2$-4), 7.38–7.53 (9H, m, NCH_2 C_6H_4CH═CH $_2$-4 and 5,6-$(CH_3)_2$-C_6H_2), 7.81 (2H, s, $NCH_2C_6H_4CH=CH_2$-4), 10.18 (1H, s, NCHN). 13 C NMR (100 MHz, DMSO-d6, 25°C): δ = 20.5 (5,6-$(CH_3)_2$-C_6H_2), 50.0 ($NCH_2C_6H_4CH$═CH_2-4), 50.2 ($NCH_2C_6H_5$), 113.9 ($NCH_2C_6H_4CH$═CH_2-4), 136.4 ($NCH_2C_6H_4CH$═CH_2-4), 115.8, 127.2, 128.6, 137.9 (5,6-$(CH_3)_2$-C_6H_2), 129.0, 129.5, 130.0, 134.1, 134.7, 137.1 ($NCH_2C_6H_4CH$═CH $_2$-4, and $NCH_2C_6H_5$), 142.0 (NCHN). This known compound was synthesized according to the literature [6].

Synthesis of 1-(4-Vinylbenzyl)-3-(3-methylbenzyl)-5,6-dimethylbenzimidazolium chloride, 1b:

1-(4-Vinylbenzyl)-5,6-dimethylbenzimidazole) was dissolved in 10 mL of DMF in a Schlenk flask. Then, 3-methylbenzyl chloride was slowly added. The mixture was stirred at room temperature for one hour and then heated to 70°C for 12 hours. After cooling to room temperature, ether was added to precipitate the solid. The obtained solid was left to crystallize in an ethanol/ether mixture. The resulting solid was washed with ether and dried under vacuum. Yield: 90%. M.p.: 237-238 °C. FT-IR ν(CN): 1661 cm^{-1}; ^{1}H NMR (399.9 MHz, DMSO-d^6, 25°C): δ = 2.30 and 2.35 (3H, s, $NCH_2C_6H_4CH_3$-3) 2.35 (6H, s, 5,6-$(CH_3)_2$-C_6H_2), 5.29 (1H, d, J = 11.2 Hz, $NCH_2C_6H_4CH=CH_2$-4), 5.72 (4H, d, J = 7.8 Hz, $NCH_2C_6H_4CH_3$-3 and $NCH_2C_6H_4CH=CH_2$-4), 5.87 (1H, d, J = 9.0 Hz, $NCH_2C_6H_4CH=CH_2$-4), 6.74 (1H, dd, J = 12.2 and 10.8 Hz, $NCH_2C_6H_4CH=CH_2$-4), 7.49 and 7.53 (8H, d, J = 8.4 Hz, $NCH_2C_6H_4CH=CH_2$-4, $NCH_2C_6H_4CH_3$-3 and 5,6-$(CH_3)_2$-C_6H_2), 7.79 (2H, s, $NCH_2C_6H_4CH=CH_2$-4), 10.05 (1H, s, NCHN). 13C NMR (100 MHz, DMSO-d6, 25°C): δ= 20.5 (5,6-$(CH_3)_2$-C_6H_2), 21.4 [$NCH_2C_6H_4CH_3$-3], 50.0 ($NCH_2C_6H_4CH=CH_2$-4), 50.2 ($NCH_2C_6H_4CH_3$-3), 113.9 ($NCH_2C_6H_4CH=CH_2$-4), 136.4 ($NCH_2C_6H_4CH=CH_2$-4), 115.8, 127.2, 128.6, 137.9 (5,6-$(CH_3)_2$-C_6H_2)), 129.0, 129.5, 130.0, 134.1, 134.7, 137.1 ($NCH_2C_6H_4CH=CH_2$-4 and $NCH_2C_6H_4CH_3$-3), 142.0 (NCHN). This known compound was synthesized according to the literature [6].

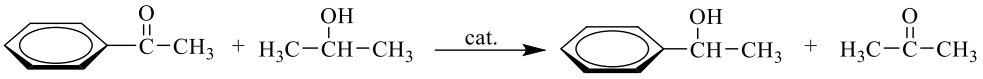
Synthesis of 1-(4-Vinylbenzyl)-3-(4-tert-butylbenzyl)-5,6-dimethylbenzimidazolium bromide, 1c:

1-(4-Vinylbenzyl)-5,6-dimethylbenzimidazole (2.62 g, 10 mmol) was dissolved in 10 mL of DMF in a Schlenk flask. Then, 4-tert-butylbenzyl bromide (2.50 g, 11 mmol) was slowly added. The mixture was stirred at room temperature for one hour and then heated to 70°C for 12 hours. After cooling to room temperature, ether was added to precipitate the solid. The obtained solid was left to crystallize in an ethanol/ether mixture. The resulting solid was washed with ether and dried under vacuum. Yield: 80%. M.p.: 252-253°C. FT-IR ν(CN): 1558 cm^{-1}; ^{1}H NMR (399.9 MHz, DMSO-d^6, 25°C): δ = 1.26 (9H, s, [$NCH_2C_6H_4C(CH_3)_3$-4]) 2.41 (6H, s, 5,6-$(CH_3)_2$-C_6H_2), 5.30 (1H, d, J = 10.8 Hz, $NCH_2C_6H_4CH=CH_2$-4), 5.73 (4H, d, J = 11.6 Hz, $NCH_2C_6H_4C(CH_3)_3$-4 and $NCH_2C_6H_4CH=CH_2$-4), 5.88 (1H, d, J = 8.8 Hz, $NCH_2C_6H_4CH=CH_2$-4), 6.74 (1H, dd, J = 12.2 and 10.8 Hz, $NCH_2C_6H_4CH=CH_2$-4), 7.44 (4H, s, $NCH_2C_6H_4CH=CH2$-4 and 5,6-$(CH_3)_2$-C6H2), 7.50 ve 7.53 (4H, d, J = 8.0 Hz, $NCH_2C_6H_4CH=CH_2$-4 and $NCH_2C_6H_4C(CH_3)_3$-4), 7.81 and 7.87 (2H, s, $NCH_2C_6H_4CH=CH_2$-4), 10.01 (1H, s, NCHN). ^{13}C NMR (100 MHz, DMSO-d^6, 25 °C): δ= 20.5 (5,6-$(CH_3)_2$-C_6H_2), 31.5 [$NCH_2C_6H_4C(CH_3)_3$-4], 34.8 [$NCH_2C_6H_4C(CH_3)_3$-4], 49.9 ($NCH_2C_6H_4CH=CH_2$-4), 50.0 [$NCH_2C_6H_4C(CH_3)_3$-4], 113.9 ($NCH_2C_6H_4CH=CH_2$-4), 136.4 ($NCH_2C_6H_4CH=CH_2$-4), 115.8, 127.2, 128.4, 137.9 (5,6-$(CH_3)_2$-C_6H_2), 129.9, 130.0, 131.8, 134.1, 137.1, 137.9 ($NCH_2C_6H_4CH=CH_2$-4 ve$NCH_2C_6H_4C(CH_3)_3$-4), 151.6 (NCHN). This known compound was synthesized according to the literature [6].

Catalytic transfer hydrogenation of ketones

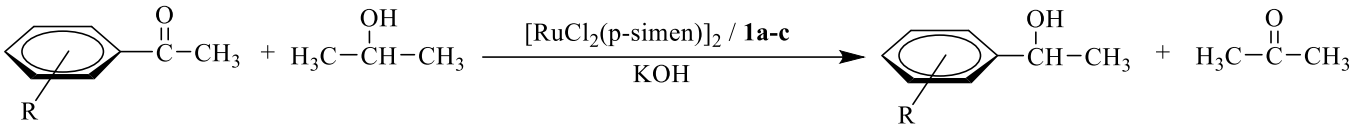
Transition-metal catalyzed transfer hydrogenation using 2-propanol as a hydrogen source has become an efficient method in organic synthesis as illustrated by several useful applications reported in recent years [7-14]. The reaction conditions for this important process are economic, relatively mild and environmentally friendly. The volatile acetone product can also be easily removed to shift an unfavorable equilibrium. Owing to its efficiency in the transfer hydrogenation of acetophenone derivatives, benzimidazole-2-ylidene salts (1a-c) were further investigated by transfer hydrogenation of various methyl aryl ketones. The benzimidazole-2-ylidene salts (1a-c) catalyzed the reduction of ketones to the

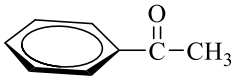
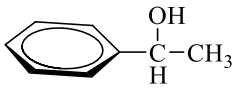
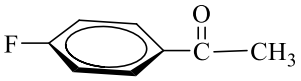
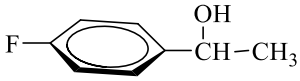
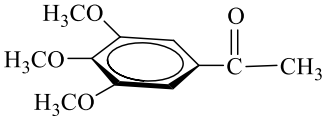
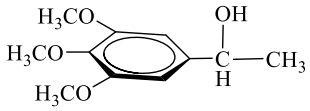
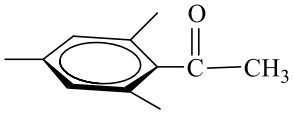
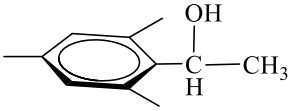
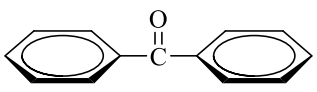
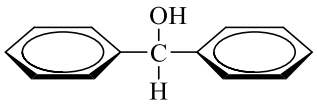
corresponding alcohols with $RuCl_2$(*p*-cymene) via hydrogen transfer from 2-propanol with KOH as the promoter. As the starting point, the performance of the catalysts in the transfer hydrogenation were screened by using acetophenone as a model substrate (eqn (1)). In a typical experiment the preformed, isolated crystalline catalyst (0.01 mmol) was dissolved in 2-propanol. After the catalysts had completely dissolved, acetophenone (1.00 mmol) and a base (4 mmol) were added and the reaction was performed at 80 ºC. The reactions were conducted at a substrate/catalyst/base (S/C/base) molar ratio of 1: 0.01: 4. In the transfer hydrogenation reaction, the base facilitates the formation of ruthenium alkoxide by abstracting proton from the alcohol and subsequently alkoxide undergoes β-elimination to give ruthenium hydride, which is an active species in this reaction. Since the base facilitates the formation of a ruthenium alkoxide by abstracting the proton from isopropanol, different bases were used as promoters in the transfer hydrogenation of ketones. Acetophenone was kept as a test substrate and allowed it to react in isopropanol with catalytic quantities of complex 2 in the presence of different bases like Cs_2CO_3, K_2CO_3, NaOH, KOH, *t*-BuOK and NaOAc. It has been observed that NaOH and KOH are shown to have good conversions when compared to the Cs_2CO_3, K_2CO_3, *t*-BuOK and NaOAc in the hydrogenation reactions. The stronger the base the higher the conversion rate, NaOAc (48%) < K_2CO_3 (56%) < Cs_2CO_3 (59%) < t-BuOK(79%) < NaOH (89) decided that base KOH is the best compromise between optimum reaction rate in isopropanol and reaching 95% conversion for acetophenone within 1 h. In the absence of a base no transfer hydrogenation of the ketones was observed [15].



(1)

Table 1. In-situ benzimidazole Ru-NHC catalyzed transfer hydrogenation of ketone derivatives



Entry	Substrate	Product	Cat.	Yield (%)
1			**1a**	98
2			**1b**	96
3			**1c**	90
4			**1a**	95
5			**1b**	90
6			**1c**	98
7			**1a**	99
8			**1b**	99
9			**1c**	90
10			**1a**	75
11			**1b**	95
12			**1c**	78
13			**1a**	60
14			**1b**	84
15			**1c**	75
16			**1a**	85
17			**1b**	79
18			**1c**	80

Reaction conditions: benzimidazol-2-ylidene salt (1a-c) (0.02 mmol), $[RuCl_2(p\text{-cymene})]_2$ (0.01 mmol) substrate (1 mmol), *i*PrOH (10 mL), KOH (4 mmol), 80 ºC, 1 h. The purities of the products were checked by GC and GC-MS and the yields were calculated according to acetophenone derivatives.

Instead of preparing carbene complexes with vinyl substituted benzimidazol-2-ylidene salts, hydrogen transfer reaction of ketones was studied by forming carbene complexes in situ conditions. [$RuCl_2$(*p*-cymene)] (0.01 mmol), benzimidazol-2-ylidene salts (1a-1c) and KOH (4 mmol) were added to the Schlenk tube under argon gas. Dry 2-Propanol (10 ml) was added and the suspension was stirred at room temperature for 30 min. Then, substrate (1 mmol) was added to the complex. It was heated at 80 ºC for 1 h. Control of the products was done by NMR spectroscopy, GC and GC-MS. Table 1 shows the yields (%) determined according to the conditions of the reactions and ketones.

IV. CONCLUSION

We successfully synthesized benzimidazolium salts (1a-1c) and elucidated their structures using appropriate spectroscopic methods. The catalytic activities of 6 different substurates of acetophenone derivatives in transfer hydrogenation reactions gave successful results. The realization of these organic reactions using environmentally friendly solvents is of great importance in terms of green chemistry. In the next step, metal complexes of these benzimidazolium salts will be synthesized and their activities in other C-C coupling reactions will be investigated.

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