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The First Report on Chemoselective Biguanide-Catalyzed Henry Reaction under Neat Conditions

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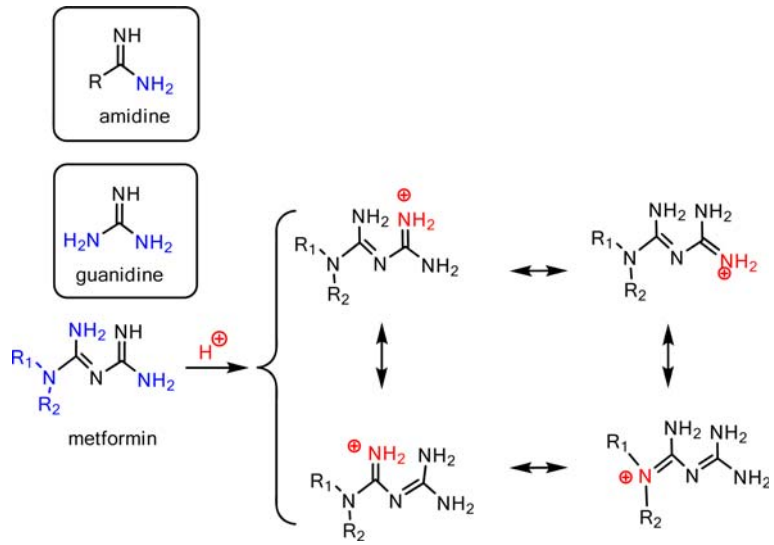
An efficient synthetic method for direct Henry reaction catalyzed by a biguanide; namely metformin, as an organosuper-base, between a variety of aromatic and aliphatic aldehydes and nitromethane under neat conditions has been developed. Convenient procedure for removal of the catalyst, chemoselective acquiring of *β*-nitroalcohols as predominant products, as far as possible short reaction time with excellent conversions are advantages of the developed protocol.

Key Words : Organosuper-base catalysts, Henry reaction, Nitroaldol reaction, Biguanides, Metformin

Introduction

One of the main purposes in organic chemistry is carbon-carbon bond formation and in this regard, the Henry reaction[1] (an aldol-type C-C bond formation; called nitro-aldol reaction) has been used extensively in many important synthetic strategies.[2] This reaction simply takes places with the help of basic organic,[3-5] inorganic catalysts[6] or quaternary ammonium salts.[7] These catalysts often result in side reactions such as aldol-condensation, Cannizzaro reaction,[8] nitroalkene formation, Michael reactions, retro-aldol reaction[1] and Nef reaction.[9] Therefore the development of new catalysts for the Henry reaction to avoid these side reactions and likewise produce nitroalchohols chemoselectively in short time, under mild conditions and using inexpensive and less toxic solvent is highly desirable.

Recently, nitrogen-containing organobases, such as amidines and guanidines, have been attracting much attention in organic synthesis due to their potential functionality.[10a-d] One of the important and beneficial characteristics of an organic base, especially from the view point of environmental aspects, is the ability of recycling use in repeated reactions, in which reversible proton transfer occurs between the base and a substrate as an acidic counterpart. Thus, powerful organic bases that may be applicable in various organic syntheses as basic catalysts have attracted much attention. Biguanides with a dual guanidine-like moiety are interesting class of organosuper-bases in which their basicity is due to the construction of a highly effective conjugation system after protonation under reversible conditions; primitively, it is a reflection of the number of canonical forms, especially isoelectronic forms, in the resonance system (Scheme 1). Generally, biguanides that contain three amino groups are stronger bases than guanidines and amidines that have two



Scheme 1. Structures of amidines, guanidines and biguanides. The number of canonical forms, in the resonance system of protonated metformin constructs a highly effective conjugation system.

and one amino groups, respectively.[11] To the best of our knowledge, whereas nitro-aldol reaction has been well studied with amines,[3] amidines[4] and guanidines,[5] there is no report on employing the biguanides in nitro-aldol reaction.

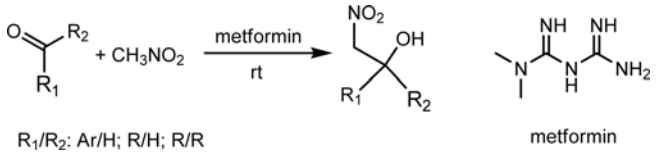
In this study, for the first time, we have utilized metformin, an easily available biguanide and very strong organosuper-base, to catalyze the Henry reaction of a variety of aliphatic, aromatic and heteroaromatic aldehydes with nitromethane at room temperature without addition of stoichiometric amount of the base.

Results and Discussion

Our investigations on the chemoselective synthesis of nitroalcohols from various aldehydes and nitromethane as a pro-nucleophile in the presence of catalytic amount of metformin, began with the optimization of the reaction conditions. The synthetic pathway is shown in Scheme 2.

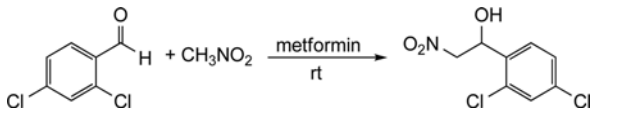
Our initial examination was involved to investigate the reaction of 2,4-dichlorobenzaldehyde with nitromethane in various conditions. Table 1 lists the representative data obtained for the synthesis of 2-nitro-1-(2,4-dichlorophenyl)-ethanol under various experimental conditions. The reaction mixture was stirred at room temperature and the progress was monitored by TLC. A control experiment in the absence of metformin (Table 1, entry 1) showed no evidence of nitroalcohol formation confirming the basic role of metformin as the organosuper-base catalyst in the described transformation.

In addition, various amounts of metformin were added under the mentioned conditions. Among different amounts of the catalyst and nitromethane (Table 1, entries 2-6), the best results were achieved when the reaction was performed with 5 mol % of catalyst and 2 equiv. of nitromethane to give 100% conversion of the starting materials to the related β-nitroalcohol product (Table 1, entry 3) and the crude ^{1}H NMR spectrum was employed to estimate yield of the desired Henry product which was ~100%. In addition, various solvents were employed for the aforementioned reaction (Table 1, entries 7-10) and high conversion was observed using nitromethane as neat conditions without the presence of solvent. Hence, the optimized conditions found for the synthesis of 2-nitroalcohols starting from aldehyde and nitromethane are the use of 1 equiv. of aldehyde, 2 equiv of nitromethane in the presence of 5 mol % of metformin at room temperature stirring for 1 h under aerobic conditions. It is worthy to mention that ^{1}H NMR studies showed no evidence of by-product formation resulting from typical side reactions such as dehydration of the 2-nitroalcohol into



Scheme 2. Henry reaction of nitromethane with carbonyl compounds catalyzed with metformin under neat condition.

Table 1. Optimization of the reaction condition



Entry	Cat. (mmol %)	CH_3NO_2 (equiv)	Solvent	Time (h)	Conversion/NMR yield (%)
1	-	2	-	24	0
2	10	2	-	2	85
3	5	2	-	1	100/100
4	2	2	-	2	45
5	5	1	-	2	50
6	10	4	-	2	90
7	5	2	H_2O	24	50
8	5	2	EtOH	24	50
9	5	2	CH_3CN	24	60
10	5	4	H_2O	24	60

nitroalkene, aldol-condensation, Cannizzaro and Nef reactions.

With a reliable set of conditions in hand, and in order to investigate the utility of metformin as an appropriate basic catalyst in Henry reaction, we also probed the scope and generality of the reaction of several aryl and alkyl aldehydes with a variety of functionalities (Table 2). As shown in Table 2, β-nitroalcohols were obtained in good to excellent conversions and the yields of the desired Henry products were estimated using the crude ^{1}H NMR spectra.

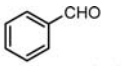
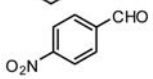
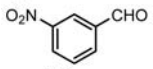
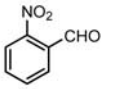
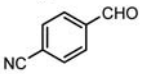
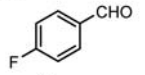
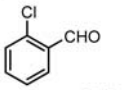
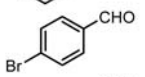
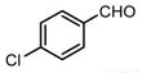
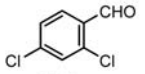
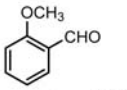
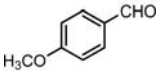
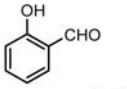
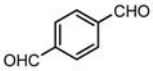
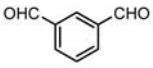
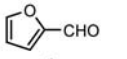
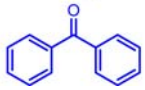
It was found that aromatic aldehydes with electron-withdrawing groups in reaction with nitromethane give the desired products with excellent conversions (Table 2, entries 2-5). When the reaction was performed with halo-benzaldehydes (Table 2, entries 6-10), the corresponding 2-nitroalcohols were obtained in good to excellent conversions ranging from 82% to 100%. Although aldehydes with electron-donating groups are more unfavorable to react rather than those with electron-withdrawing groups however they gave the desired products in high to excellent conversions (Table 2, entries 11-13) which showed that the nature of the substitutions on the ring did not significantly hamper the reaction.

In addition, reaction of di-aldehydes such as iso- and terephthalaldehyde with nitromethane under the developed conditions led to the related di-β-nitroalcohols (Table 2, entries 14, 15) through double cascade Henry reactions. Interestingly, heteroaromatic aldehydes reacted with the nitromethane and gave their related β-nitroalcohols with 100% conversions (Table 2, entries 16, 17).

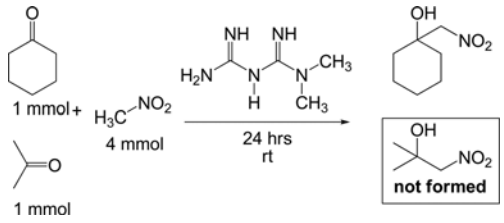
Due to the possible self-condensation reaction of aliphatic aldehydes, they seem to be less reactive in Henry reaction. Notably, under the developed protocol the biguanide-type catalyst was capable of catalyzing the Henry reaction of an aliphatic aldehyde with nitromethane and chemoselective acquiring of β-nitroalcohols in high to excellent conversions (Table 2, entry 18).

The scope of the developed procedure was more expand-

Table 2. Henry reaction between various aldehydes (1 mmol) and nitromethane (2 mmol) using 5 mol % of catalyst at room temperature for 1 h

Entry	Aldehyde	Conversion (%)	NMR Yield (%)
1		100	~ 100
2		100[b]	–
3		100[b]	–
4		100[b]	–
5		95	–
6		95	90
7		100	100
8		88	88
9		82	75
10		100	100
11		98	95
12		90	–
13		70	66
14		100	100
15		100	100
16		100	85
17		100	90
18		79	73
19		100	100
20		N.R.[c]	–
21		N.R.[c]	–
22		N.R.[c]	–

[a]Determined by ^{1}H NMR. [b]Completed after 15 min. [c]No reaction after 24 h.



Scheme 3

ed, especially on ketone substrates. In order to evaluate the possible catalytic activity of biguanide in the Henry reaction of ketones, we probed the reaction of various aliphatic, aromatic, and aryl-alkyl ketones with nitromethane. Among the studied ketones, only cyclohexanone showed the excellent reactivity in short time (Table 2, entry 19) while acetone, acetophenone and benzophenone failed to give the desired products under the developed condition (Table 2, entries 20-22) possibly due to the preferential self-condensation reaction or retro-Henry reaction.[12] The Henry reaction with ketones is sensitive to steric factors and generally gives a complex mixture of products depending on the ratio of reactants, base, temperature and time.

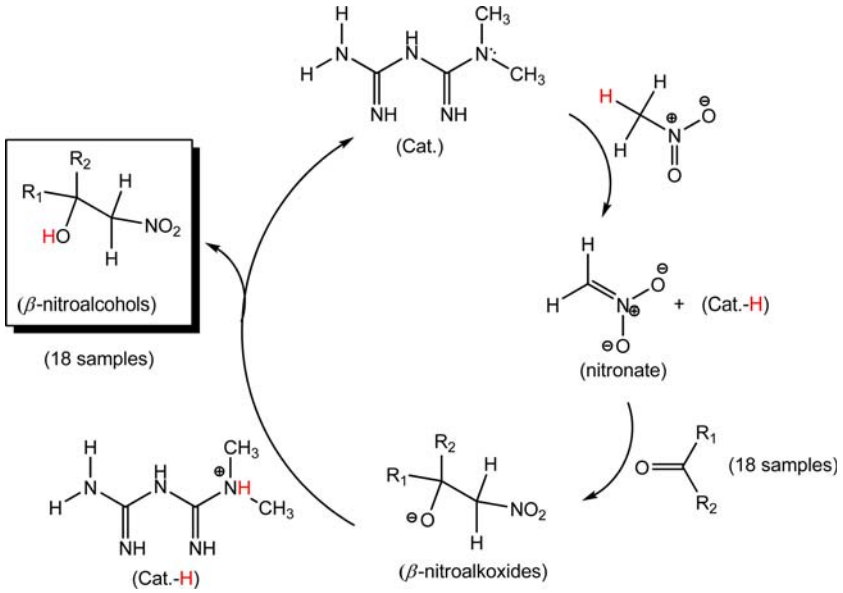
To provide more experimental supports for the above-mentioned chemoselectivity, we mixed 1 mmol of acetone, 1 mmol of cyclohexanone with excess amount (4 mmol) of nitromethane and stirred the mixture overnight at room temperature (Scheme 3). Interestingly, the desired Henry product was only obtained from cyclohexanone and acetone was obtained unreacted.

A plausible reaction mechanism is shown in Scheme 4. The attack of metformin (Cat.) *via* its most basic site (dimethylamino moeity) on nitromethane (pro-nucleophile) with acidic protons leads to the formation of nitronate anion (nucleophile) which consequently can attack to the aldehyde derivatives to give β-nitroalkoxides followed by the abstraction of an hydrogen from the protonated form of catalyst (Cat.-H) to yield the corresponding β-nitroalcohols and recovered catalyst.

In conclusion, metformin; as an organosuper-base with a considerable basicity was used in Henry reaction without drove the reaction to unfavorable side reactions such as Cannizzaro, aldol condensation or Nef transformations. It should be underlined that the reaction has been green since no organic solvent was consumed in reaction and at the end of the reaction, the catalyst was easily separated. Convenient procedure for removing the catalyst, chemoselective acquiring of β-nitroalcohols as predominant products as far as possible short reaction time with excellent conversions are advantages of the developed protocol. Eventually, we summarized our comparative study between existing catalysts and metformin in Table 3.

Experimental

The commercially available starting materials were all reagent-grade materials and used without further purification. Throughout all experiments distilled water was used and all



Scheme 4. Representative mechanism of metformin-catalysed Henry reaction of aldehydes and ketones with nitromethane.

Table 3. Comparative results for the synthesis of *β*-nitroalcohols using the reported methods versus the present method (Entry 8)

Entry	Catalyst/Promoter	Aldehydes/nitroalkane	Conditions	Yield (%)	Ref.
1	NaOH 0.025 M (3 mL)	Benzaldehyde & nitromethane	CTACl (0.1 mmol), rt/2 h	70	6b
2	(Mg:Al=3:1) HT (19-30 mg)	Benzaldehyde (0.5 mmol), nitromethane (0.75 mmol)	[bmim][BF_4] (1 mL) 60 °C/10 h	64	13a
3	[TMG][F_3Ac] IL (1 g)	Benzaldehyde (5 mmol), nitromethane (100 mmol)	20 °C/20 h	55	13b
4	Mg:Al 2:1 HT	Benzaldehyde (5 mmol), nitromethane (100 mmol)	20 °C/5 h	80	13c
5	TMG (10%)	Benzaldehyde (1 mmol), nitromethane (1 mmoll)	rt/1 h	73	10d
6	Cyclen (5 mol %)	Benzaldehyde (1 mmol), nitromethane (2 mmol)	THF (1 mL), 24 h	80	3b
7	Ultrasound	Benzaldehyde (1 mmol), nitromethane (3 mmol)	ammonium acetate (0.2 mmol), 60 °C/45 min	57	14
8	Present work	Benzaldehyde (1 mmol), nitromethane (2 mmol)	rt/1 h	97	-

the experiments were done at room temperature. ^{1}H NMR spectra were recorded on a Bruker 200 MHz spectrometers in deuteriochloroform solution and are reported in parts per million with respect to chloroform peak at 7.26 ppm. ^{13}C NMR spectra were recorded either on a Bruker 200 MHz spectrometers in deuteriochloroform solution and are reported in parts per million with respect to chloroform peak at 77.0 ppm. The units of the coupling constants (*J*) are given in Hz. Melting points were measured on a BI Branstead Electrothermal 9200 instrument and are uncorrected. FT-IR spectra were recorded on a Rayleigh Wqf-510 spectrometer using a drop casting technique on KBr plates and are reported in wave numbers (cm^{-1}). Mass spectra and exact masses were recorded on a MAT 8200 Finnigan high-resolution mass spectrometer.

Preparation of Free Metformin. To a solution of NaOH (40 mg, 1 mmol) in ethanol (5 mL) was added metformin hydrochloride (165.5 mg, 1 mmol) and the resulting suspension was stirred for 1 h. Then, this suspension was filtered, and ethanol was removed from the filtrate with rotary evaporation leading to free metformin in 99% yield. The obtained free metformin was freshly used in the next experiments.

General Procedure for the Henry Reaction of Nitromethane and Various Aldehydes. A mixture of the aldehyde (1 mmol) and nitromethane (2 mmol) and metformin (5 mol %) was stirred at room temperature for 1 h. After completion (monitored by TLC), the product was extracted with diethyl ether (3 mL). Then, the resulting organic phase was washed copiously with distilled water and evaporated to give the appropriate *β*-nitroalcohol as only final product. The known products were characterized by comparing the ^{1}H NMR and melting point data with those reported in the literature (for references see Supplementary Data). Selected characterization data for some of the *β*-nitroalcohols prepared are given below.

2-Nitro-1-phenylethanol[15a-f]. Light yellow oil; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 3.48 (1H, br s, OH), 4.36-4.7 (2H, m, CH_2), 5.31-5.38 (1H, m, CH), 7.23-7.59 (5H, m). ^{13}C NMR (50.03 MHz, $CDCl_3$) δ 70.6, 80.8, 125.7, 128.5, 128.6, 138.1. HRMS (EI): *m/z* Calcd. For $C_8H_9NO_3$: 167.0582, Found: 167.0546.

2-Nitro-1-(4-nitrophenyl)ethanol[15a-e,16]. Light yellow solid;

mp 81 °C [lit.[14e] mp 82-83 °C]; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 3.12 (1H, br s, OH), 4.55-4.59 (2H, m, CH_2), 5.50-5.65 (1H, m, CH), 7.61 (2H, d), 8.28 (2H, d). ^{13}C NMR ($CDCl_3$, 50 MHz) δ 69.6, 80.1, 123.8, 126.7, 145.1, 148.0. HRMS (EI): *m/z* Calcd. For $C_8H_8N_2O_5$: 212.0433, Found: 212.0412.

1-(2,4-Dichlorophenyl)-2-nitroethanol[15c]. Colorless oil; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 3.55 (1H, br s, OH), 4.42-4.74 (2H, m, CH_2), 5.84-5.90 (1H, m, CH), 7.29-7.99 (4H, m, Ar). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 67.4, 79.1, 127.9, 128.5, 129.5, 132.0, 134.2, 135.2. HRMS (EI): *m/z* Calcd. For $C_8H_7Cl_2NO_3$: 234.9804, Found: 234.9826.

1-(2-Methoxyphenyl)-2-nitroethanol[15c-d,f]. Light yellow oil; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 3.63 (1H, br s, OH), 3.77-3.88 (3H, m, OCH_3), 4.43-4.61 (2H, m, CH_2), 5.55-5.61 (1H, m, CH), 6.86-7.40 (4H, m, Ar). ^{13}C NMR ($CDCl_3$, 50 MHz) δ 67.6, 79.8, 110.4, 121.0, 125.9, 127.1, 129.7, 155.9. HRMS (EI): *m/z* Calcd. For $C_9H_{11}NO_4$: 197.0688, Found: 197.0617.

1-(2-Pyridyl)-2-nitroethanol[3b]. Light yellow oil; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 4.40 (1H, br s, OH), 4.64-4.78 (2H, m, CH_2), 5.47 (1H, m, CH), 7.29 (1H, m), 7.44 (1H, m), 7.76 (1H, m), 8.57 (1H, m). ^{13}C NMR ($CDCl_3$, 50 MHz) δ 70.3, 80.7, 120.9, 123.6, 137.4, 148.9, 156.5. HRMS (EI): *m/z* Calcd. For $C_7H_8N_2O_3$: 168.0535, Found: 168.0555.

1-(Furan-2-yl)-2-nitroethanol[15a,c-f]. Dark yellow oil; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 2.99 (1H, br s, OH), 4.61-4.81 (2H, m, CH_2), 5.47 (1H, m, CH), 6.86-7.40 (4H, m). ^{13}C NMR ($CDCl_3$, 50 MHz) δ 64.7, 78.3, 108.1, 110.6, 143.1, 150.7. HRMS (EI): *m/z* Calcd. For $C_6H_7NO_4$: 157.0375, Found: 157.0311.

1-Nitropentan-2-ol[17,18]. Colorless oil; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.93-0.97 (m, 3H), 1.41-1.59 (m, 4H), 2.52 (brs, 1H), 4.00-4.47 (m, 3H). ^{13}C NMR ($CDCl_3$, 50 MHz) δ 13.7, 18.4, 35.7, 68.4, 80.6. HRMS (EI): *m/z* Calcd. For $C_5H_{11}NO_3$: 133.0739, Found: 133.0777.

1-(Nitromethyl)cyclohexanol[13d]. Colorless oil; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.38-1.64 (10H, m, CH_2, 2.78 (1H, br s, OH), 4.37 (2H, s, CH_2). ^{13}C NMR ($CDCl_3$, 50 MHz): 21.5, 27.1, 40.1, 64.3, 80.2. HRMS (EI): *m/z* Calcd. For $C_7H_{13}NO_3$: 159.0895, Found: 159.0874.

1,1'-(1,4-Phenylene)bis(2-nitroethanol). White-off solid; mp 165 °C; ^{1}H NMR (DMSO-d_6, 200 MHz) δ 4.38-4.57 (2H, m, CH_2), 4.77-4.84 (2H, m, CH_2), 5.20-5.25 (2H, m, CH), 6.04-6.07 (2H, OH), 7.39 (4H); ^{13}C NMR (DMSO, 50 MHz) δ 69.7, 81.6, 126.3, 140.2; MS *m/z* (relative intensity %): 256 (M^+), 148 (100), 133 (40), 103 (30), 91 (25), 77 (35), 51 (10). HRMS (EI): *m/z* Calcd. For $C_{10}H_{12}N_2O_6$: 256.0695, Found: 256.0672.

1,1'-(1,3-Phenylene)bis(2-nitroethanol). Yellow oil; ^{1}H NMR (DMSO-d_6, 200 MHz) δ 4.53-4.66 (2H, m, CH_2), 4.81-4.91 (2H, m, CH_2), 5.29-5.36 (2H, m, CH), 6.21-6.23 (2H, OH), 7.32-7.67 (3H, m), 7.79 (1H, s); ^{13}C NMR (DMSO, 50 MHz) δ 69.6, 81.4, 121.0,127.0, 129.6, 140.2; MS *m/z* (relative intensity %): 256 (M^+), 252 (75), 209 (45), 191 (30), 161 (45), 148 (60), 133 (98), 117 (100), 103 (55), 91 (75), 77 (50), 51 (15). HRMS (EI): *m/z* Calcd. For $C_{10}H_{12}N_2O_6$: 256.0695, Found: 256.0618.

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