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Pd/C–Catalyzed Selective *N*-Monomethylation by Transfer Hydrogenation of Urea Derivatives using Methanol as H_2 and C1 Sources

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N-monomethyl amines are useful intermediates in drugs, natural products, paints. Yet their synthesis is a tremendous challenge due to their high reactivity, typically leading to overmethylation. In this contribution, a highly selective catalytic *N*-methylation methodology is reported, converting urea derivatives to monomethylated amines, using a commercially available heterogeneous Pd/C catalyst and methanol as unique reagent. Methanol provides a sustainable alternative protocol for the selective preparation of mono-methylated derivatives as it acts as both H_2 and C1 sources. In addition, several control experiments were performed to provide a proposal for the mechanism, namely dehydrogenation of methanol and subsequent hydrogenation of urea derivatives, followed by reduction of the *in situ* formed methyl imine. Importantly, the approach is simple, highly productive and enables novel synthetic procedures for the preparation of monomethylamines from urea derivatives.

Introduction

N-methylated amines play an important functional role in surfactants, dyes, biological, and pharmaceutical compounds.[1] *N*-methylated moieties are also widely employed in compounds relevant for biomedical research and drug discovery[1,2] as *N*-methylated drugs are useful owing to their robust activity.[2b,3] In general these compounds are not readily accessible by simple alkylation reactions as the *N,N*-dimethylated is the main product over the *N*-monomethylated analogue due to the higher reactivity of monomethylamines compared to amines.[4] In addition, alkylating reagents such as methyl iodide are more toxic.[5] Therefore, sustainable synthesis protocols that lead to selective monomethylated amine products are highly desirable. In this context, the Chiappe group reported the synthesis of *N*-monomethylated amines via alkylation using MeI in [bmim][PF_6] ionic liquid, but only for a narrow range of substrates.[6] The Dalcanale group reported the application of a tailor made supramolecular host, a tetraphosphonate cavitand, which also resulted in alkylation without over-methylation.[7] Alternative synthetic routes have been reported via cheap C1 carbon sources such as Carbon dioxide,[8] formaldehyde,[9] formic acid[10] and dimethyl carbonate[11] also leading to the selective preparation of *N*-monomethylamines. Among all the environmentally friendly methylating reagents, methanol has emerged as an attractive carbon source.[12] Accordingly, *N*-monomethylation of primary amines with methanol is highly sought after and remains to be a challenge. To achieve *N*-monomethylation of various amines using methanol as the carbon source homogeneous catalysts containing Ruthenium,[13] Iridium,[14] Rhenium,[15] Palladium,[16] Iron,[17] Manganese,[18] and Cobalt[19] with suitable ligands and heterogeneous catalysts based on iridium,[20] Pt/C,[21] Pd/C,[22] Ni,[23] Co nanoparticles[24] were also employed. Further, one-pot conversion of nitroarenes into *N*-methylarylamines employing methanol with palladium phosphine complexes,[25] Ruthenium complexes,[26] Iridium complexes,[27] complexes based on manganese,[28] and other heterogeneous catalysts[21,29] have been reported with moderate yield.

Recently, Natte published the formation of N-methylated products from nitroarenes and amines by using commercially available Pd/C catalyst using hydrogen and methanol as C1 sources (Scheme 1a).[22a] The above protocols all rely on the conversion of nitro and amine derivatives as starting material for formation of *N*-monomethylated amines. The formation of monomethylamine compounds from catalytic cleavage of urea provides an interesting alternative. First of all, these urea compounds are accessible *via* sustainable protocols from amines and CO_2. More importantly, in total synthesis urea groups can be used as protective groups, and these can be considered as masked *N*-monomethylated amines if suitable transformations are available. However, it is difficult to control the selectivity between C–O bond and C–N bond cleavage in

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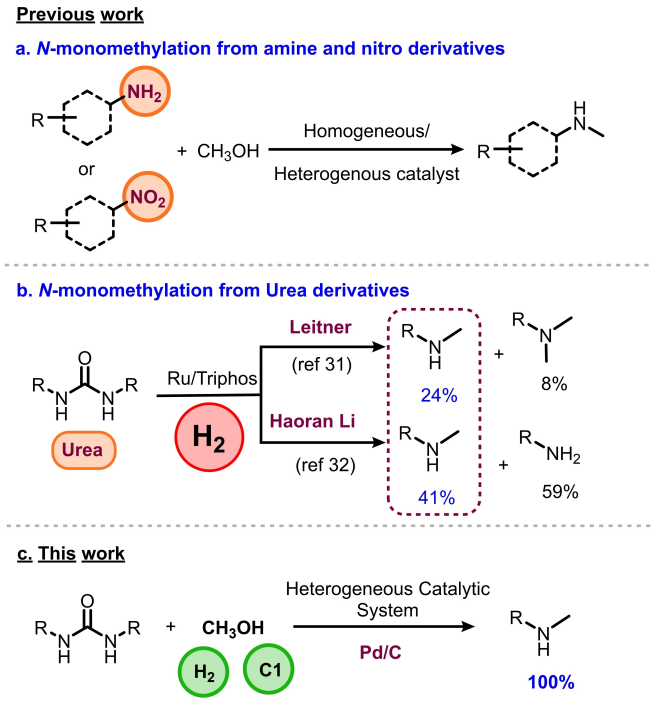


Scheme 1. a) Methyl amine formation from amine and nitroarene compounds b) Methyl amine formation by hydrogenation of urea derivatives c) Present work demonstrates highly selective *N*-monomethylation from urea through transfer hydrogenation using methanol.

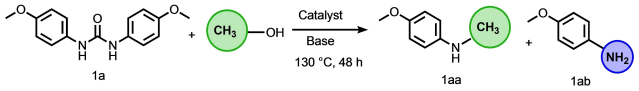
carbonic acid derivatives, the typical challenge in this transformation.[30] Leitner and co-workers achieved 24% of monomethylamine formation from diphenylurea by hydrogenation using the Ru/triphos system.[31] Very recently, with the same catalytic system monomethylation of most urea derivatives has been reported to reach 41% yield of monomethylated product and 59% of amine using high pressure of hydrogen where the carbonyl group of urea served as the C1 source.[32] In the light of the importance of the sustainable production of *N*-monomethyl amines with high selectivity, we explored whether these compounds are accessible *via* a Acceptorless Dehydrogenative Coupling (ADC) strategy.

This strategy uses methanol as a hydrogen source by dehydrogenation, as well as a sustainable C1 source. Moreover, the dehydrogenation protocol can be performed at ambient pressure.[33] Herein, we report the first efficient heterogeneous catalytic system for the highly selective formation of *N*-monomethyl amines from urea derivatives in methanol. This is achieved by using a commercially available Pd/C catalyst, and mechanistic studies indicate that the process is based on the dehydrogenation of methanol, hydrogenation of urea followed by hydrogenation of the resulting imines to form the *N*-monomethylated amine.

Results and Discussion

1,3-Bis(4-methoxyphenyl)urea (**1 a**) was selected as a model substrate for the study of hydrogenation followed by methylation of aryl ureas. In our initial exploration to find proper conditions various catalysts were used and *t*-buOK (0.6 mmol) in the presence of methanol (2 ml) at 130 °C for 48 h (Table 1, entries 1–4). From the different catalysts, Rh/C and Ru/C (Table 1, entries 1,3) resulted in formation of *p*-anisidine **1 ab** in 42% and 38% yield respectively, hence with poor selectivity towards methylated product **1 aa**. Only 17% of *p*-anisidine **1 ab** was observed using activated carbon as a catalyst (Table 1, entry 4). Interestingly, *N*-methylation of **1 a** resulted in 99% yield of methylated product **1 aa** using Pd/C (10 mg) as catalyst (Table 1, entry 2). Thus, by using Pd/C as catalyst the methylation reaction is much more selective than for other metals. Furthermore, changing the base from *t*-buOK to carbonates or acetates (Table 1, entries 5–7) resulted in lower yield of **1 aa** whereas moderate yield was obtained when KOH and NaOH were used as base (Table 1, entries 8,9). The Catalyst Pd/C is essential for the methylation reaction (Table 1,entries 2, 10). With Pd/C catalyst (5 mg), the methylated product decreased to 47% of yield (Table 1,entry 11). On decreasing the *t*-buOK loading to 0.4 mmol, resulted in lower yields as only 82% of **1 aa** was obtained as lower amount of base is not sufficient to carry out hydrogenation of substrate and subsequent methylation. (Table 1, entry 12 vs entry 2). Reducing the reaction temperature to 100 °C resulted in substantial loss of yield and selectivity, 55% of desired product was detected (Table 1, entry 13). Shorter reaction times were explored and for 24 h reaction 46% yield of *p*-anisidine **1 ab**, and only 54% yield of monomethylated product **1 aa** were obtained [Table 1, en-

Table 1. Exploration of *N*-monomethyl amine formation from urea derivatives.



Entry[a]	Catalyst	Base	1aa[b]	1ab[b]
1	Rh/C	*t*-buOK	–	42%
2	Pd/C	*t*-buOK	99%	–
3	Ru/C	*t*-buOK	–	38%
4	Carbon	*t*-buOK	–	17%
5	Pd/C	Na_2CO_3	11%	24%
6	Pd/C	K_2CO_3	30%	54%
7	Pd/C	CH_3CO_2K	36%	15%
8	Pd/C	KOH	78%	–
9	Pd/C	NaOH	70%	–
10	Nil	*t*-buOK	–	20%
[c]11	Pd/C	*t*-buOK	47%	23%
[d]12	Pd/C	*t*-buOK	82%	–
[e]13	Pd/C	*t*-buOK	55%	44%
[f]14	Pd/C	*t*-buOK	52%	46%

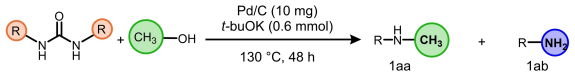
[a] Conditions: *p*-OMe urea (0.2 mmol), catalyst (10 mg- 4.7 mol%), base (0.6 mmol) and Methanol (2 mL), heated in oil bath at 130 °C for 48 h. [b] Yields and conversions determined by GC analysis using mesitylene as internal standard. [c] Pd/C 5 mg, [d] *t*-buOK 0.4 mmol, [e] temp 100 °C, [f] time 24 h.

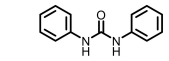
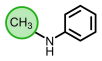
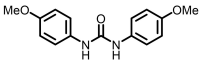
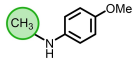
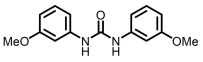
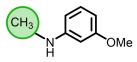
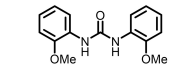
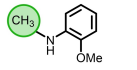
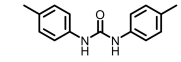
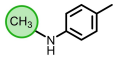
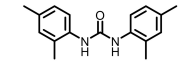
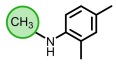
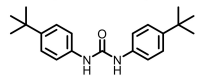
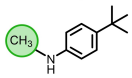
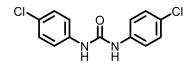
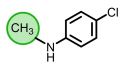
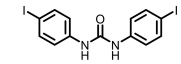
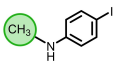
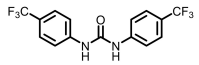
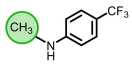
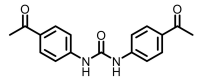
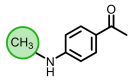
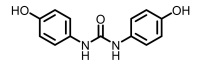
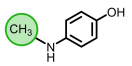
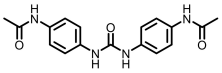
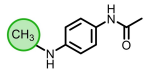
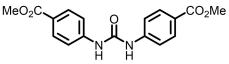
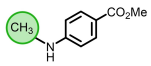
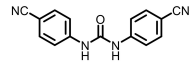
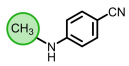
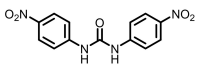
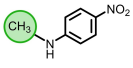
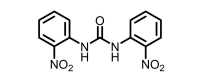
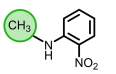
try 14]. Also, the time course experiments were analysed (SI-Figure S6). Apparently, the overall reaction required 48 h to get monomethylated **1 aa** in high yields. To summarize, the optimal reaction condition was the application of 4.7 mol % of Pd/C, 0.6 mmol of *t*-BuOK and 2 mL of methanol at 130 °C for 48 h, leading to the selective formation of *N*-monomethylated amines from the urea substrate.

We next explored the scope of the urea substrates under the optimized conditions (Table 2). An electron-donating group at the *para* position of aromatic substituted urea enhanced the reactivity of the urea substrates (Table 2, entries 2–3) compared to the diphenyl analogue (Table 2, entry 1). Among these 1,3-Bis(4-methoxyphenyl)urea shows excellent yield of 95% (entry 2) but *meta* and *ortho* methoxy substituted ureas resulted in lower yields of the product 76% and 54%, respectively (Table 2, entries 3 and 4). Substrates with alkyl groups on the phenyl moiety of the urea where also converted smoothly, with decreasing yields going from *para*-methyl, dimethyl to *t*-butyl groups with corresponding yields of methylated products of 92%, 72% and 69% respectively (Table 2, entries 5–7). Similarly, substrates with an electron-withdrawing groups like chloro, iodo and CF_3 at *para* position were converted in good yields of 82%, 90% and 50% (Table 2, entries 8–10). On the other hand, many other functional groups were tolerated; alcohol and acetamide bearing phenyl urea substrates were converted with 55% and 50% yields (Table 2, entries 11–13), but no reaction occurs in the case of ester functional group (Table 2, entry 14). Moderate yield was obtained in the case of *p*-ketone, *p*-CN, *p*-NO_2 and *m*-NO_2 (Table 2, entries15–17). Urea derivatives based on cyclohexyl were again converted with good yield of 82% (Table 3, entry 18). Apart from cyclohexyl urea, no conversion was observed for other aliphatic ureas like in 1,3-dibutyl urea (Table 3, entry 19). Heteroatom-containing substrates like 1,3-Di(pyridine-3-yl)urea did not give the desired product (Table 3, entry 20). This might be due to the coordination of the heteroatom lone pair to the metal center, which might inhibit the reaction. Whereas unsymmetrical urea derivatives follow a different protocol, which is an ongoing work to be reported as a separate article. Next, we performed the direct *N*-monomethylation of **1 a** on 0.5 g scale and 70% of the desired product was isolated (Scheme 2).

A series of control experiments were explored to shine light on the mechanism by which the protocol leads to selective *N*-monomethylated products. First and foremost, the generation of hydrogen gas was confirmed by GC (Figure S1), by the dehydrogenation of methanol under the standard conditions as it is also formed in absence of the substrate (Scheme 3A). Using deuterated methanol led to the formation of the deuterated methyl amine product as shown by NMR and HRMS (Figure S2 & S3), indicating that methanol acts as hydrogen and C1 source (Scheme 3B). In order to analyze the intermediate products of this reaction the reaction was monitored in time. After 3 h, 48% of unreacted urea was observed but after 6 h, 30% of aniline (**1 ab**) and 17% of *N*-methylaniline (**1 aa**) were obtained. On increasing the reaction time, gradually aniline (**1 ab**) was converted to *N*-methylaniline (**1 aa**). Accordingly, within 24 h 46% of monomethylated product and 54% of aniline product

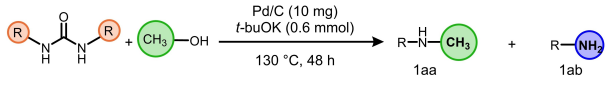
Table 2. Pd/C catalyzed *N*-monomethylation of various Urea derivatives with methanol.

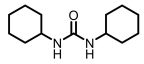
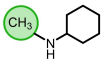
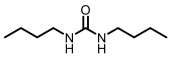
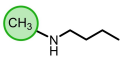
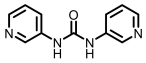
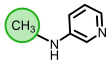


Entry	Urea derivative	N-me aniline	Yields[b]
1			70%
2			95%
3			76%
4			54%
5			92%
6			72%
7			69%
8			82%
9			90%
10			50%
11			52%
12			55%
13			50%
14			nd
15			62%
16			45%
17			30%

[a] Conditions: urea derivative (0.2 mmol), catalyst (10 mg), base (0.6 mmol) and Methanol (2 mL), 130 °C, 48 h. Products were detected by the NMR. [b] Yield of isolated product. nd – not detected.

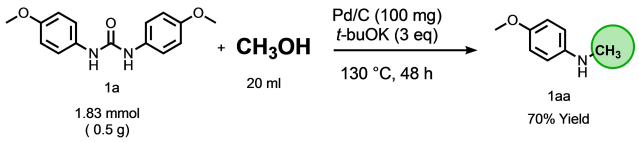
Table 3. Pd/C catalyzed *N*-monomethylation of aliphatic and heteroatom based urea derivatives with methanol.



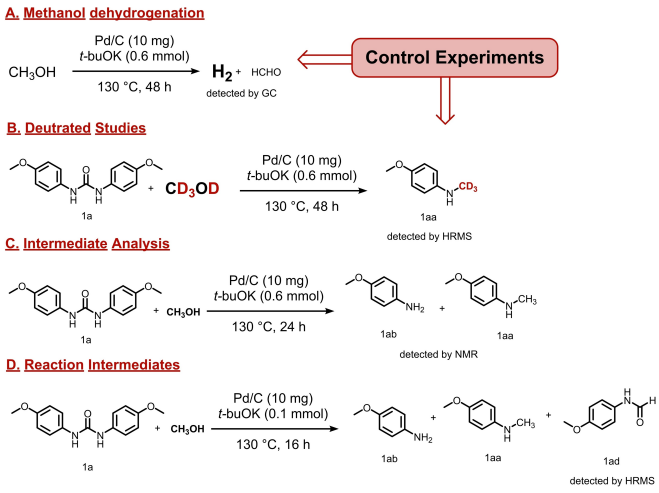
Entry	Urea derivative	N-me aniline	Yields[b]
18			82%
19			nd
20			nd

[a] Conditions: urea derivative (0.2 mmol), catalyst (10 mg), base (0.6 mmol) and Methanol (2 mL), 130 °C, 48 h. Products were detected by the NMR. [b] Yield of isolated product. nd – not detected.

Gram-Scale Synthesis



Scheme 2. Gram scale synthesis.



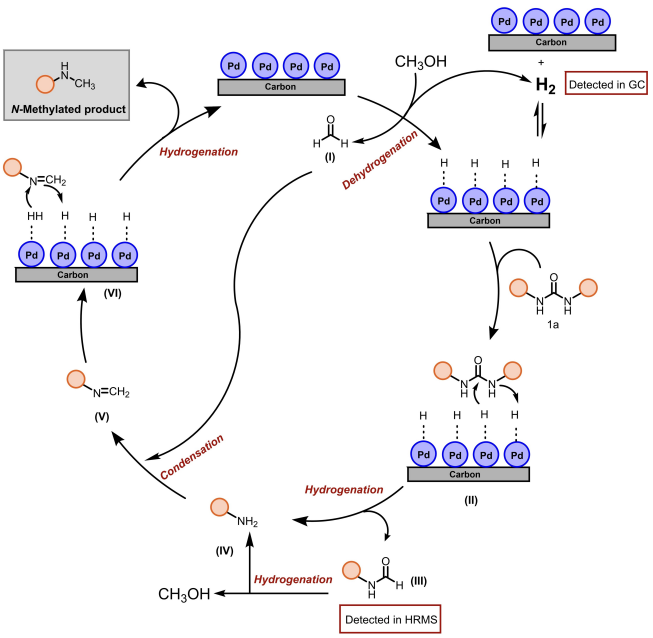
Scheme 3. Control experiments that provide information on the mechanism. [A] Methanol dehydrogenation as detected by GC [B] Deuterated methanol led to deuterated product [C] Analysis of intermediates show aniline and methyl aniline [D] Reaction Intermediates detected by HRMS show also the phenylformamide as intermediate.

were observed by NMR (Scheme 3C, Figure S4). Selective formation of the *N*-methylaniline (**1 aa**) was observed after 48 h, indicating that all aniline was converted. This reaction time experiment shows that aniline (**1 ab**) acts as one of the intermediates in this transformation.

Finally, we conducted *in situ* HRMS experiments to identify further intermediates, which indicated the presence of *N*-phenyl formamide after a reaction time of 16 h (Scheme 3D, Figure S5). Primary kinetic isotope effect (KIE) experiment were carried out to determine the rate-determining step (Table S1, Figure S7). Reactions using an equimolecular mixture of methanol or methanol-d_4 resulted in a KIE of $K_H/K_D = 3.4$, thereby confirming the methylation route to the production of hydrogen from methanol as the rate-limiting step for the subsequent C–N bond cleavage of urea. Based on the information provided by these control experiments, a proposed mechanism for the selective formation of *N*-monomethylated products from urea derivatives is proposed and depicted (Scheme 4). Initially, hydrogen and formaldehyde are produced through the methanol dehydrogenation[26a,34] in the presence of Pd/C and *t*-buOK. The active Pd–H intermediate is formed with this hydrogen, which reacts with urea to give the corresponding *N*-phenylformamide **(III)** and aniline **(IV)**. Consecutively, *N*-phenylformamide **(III)** can be hydrogenated to form aniline **(IV)**. The aniline **(IV)** forms the imine **(V)** *via* condensation with formaldehyde **(I)**,[21] from methanol. The imine intermediate could not detected through characterization studies. We believe that the immediate hydrogenation **(V)** of imine product, results in too low concentrations of the intermediate for detection. Then imine **(V)** undergoes hydrogenation, which gives the desired product *N*-methylaniline and regenerates the Pd metal sites on the catalyst surface.

Conclusions

In summary, we report a simple protocol for the highly selective formation of *N*-monomethylated products from urea deriva-



Scheme 4. Proposed reaction mechanism for the Pd/C catalyzed *N*-monomethylated amine formation from urea substrates.

tives. It is at ambient pressure using methanol as the hydrogen and carbon source, in the presence of commercially available Pd/C catalysts. Mechanistic studies suggest that the catalyst first dehydrogenates methanol, and hydrogenates the urea substrate, accomplishing a formal transfer-hydrogenation of urea derivatives. The amines form imines with the formed formaldehyde, which after hydrogenation lead to monomethylated amines. This is the first report of a Pd/C heterogenous catalyst that forms *N*-monomethylated from organic urea derivatives with 100% selectivity, and a relevant substrate scope. Interestingly, methanol acts as the H_2 and C1 source. The simplicity of the protocol facilitates the future industrial scale synthesis of ***N*-monomethyl amines**.

Supporting Information Summary

The authors have cited additional references within the Supporting Information.[35] The Supporting Information includes Experimental details, characterization data of compounds and control studies (PDF).

Acknowledgements

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: *N*-monomethyl amine formation · Urea conversion · Methanol · Transfer Hydrogenation · Heterogeneous catalysis · Pd/C catalyst

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