Synlett D. B. Nale, B. M. Bhanage Letter

An Efficient Protocol for Formylation of Amines Using Carbon Dioxide and PMHS under Transition-Metal-Free Conditions

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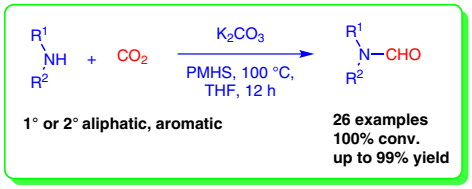

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Abstract A highly efficient, green and simple base catalytic system was investigated for the formylation of amines using CO_2 and PMHS [poly(methylhydrosiloxane)] under mild reaction conditions. This reaction proceeds smoothly without additives and furnishes the corresponding N-formylated products from both the 1° and the 2° aliphatic as well as aromatic amines in good to excellent yields.

Keywords amine, carbon dioxide, formamides, formylation, potassium carbonate

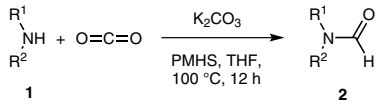
Carbon dioxide is a ubiquitous C1-building block in synthetic chemistry.[1] A green route for the forrmylation of amines employs CO_2 along with poly(methylhydrosiloxane) (PMHS) and the development of this technology has generated long-term interest from both academic and industrial viewpoints.[2] However, due to the inherent thermodynamic and kinetic stability of CO_2, its activation is challenging, especially under mild conditions. It has been reported that alkali carbonates[3] and hydrosilanes can activate CO_2 under mild conditions in the presence of amines to form the corresponding carbamic acids.[4] However, the scope of CO_2 chemical transformations in industrial applications is restricted to areas such as the synthesis of urea, cyclic and polymeric carbonates, formic acid, methanol and salicylic acid.[5] An improvement in such synthetic procedures would be to avoid the use of transition-metal catalysts. Transition-metal-free reactions have gained considerable attention in organic synthesis, especially in hydrosilylation reactions.[6]

PMHS is an abundant waste product of the silicone industry; is nontoxic, biodegradable, moisture-stable, and inexpensive. PMHS has been used as an environmentally benign reductant for CO_2 and serves as an efficient energy source as well.[5h,7] In fact, hydrosilanes (Si-H) and molecular hydrogen (H_2) have a similar reduction potential as the Si–H bond is kinetically more reactive (due to its polarity and lower bond dissociation energy, i.e. 92 kcal mol^{-1} in SiH_4 and 104 kcal mol^{-1} in H_2).[8]

Formamides have widespread applications as solvents, raw materials and versatile intermediates in various synthetic processes, especially as precursors to isocyanides and formamidines.[9] The formamide moiety can impart high biological activity in various pharmaceuticals.[10] The formylation of dimethylamine using CO_2 to form *N*,*N*-dimethylformamide (DMF) has gained considerable industrial attention using homogeneous or heterogeneous catalysis.[2a,c,d,11–14] Conventionally, formamides are synthesized using carbon monoxide as the carbonyl source under forcing conditions with sodium methoxide as a catalyst.[15] Baiker et al.[16] and Beller et al.[17] have reported that non-precious metal complexes demonstrate higher activities in the hydrogenation of CO_2 for the production of DMF. The reducing characteristics of hydrosilanes have been used to convert CO_2 to carboxylic acids, formamides and methylamines.[13b–e,13i,j,18,19]

However, most of the existing methodologies have some disadvantages such as requirement for toxic reagents, such as phosgene or CO, expensive metal phosphine complexes and often require forcing reaction conditions. Hence, there is still a need to develop a transition-metal-free protocol for the synthesis of formamides from aliphatic as well as aromatic amines using CO_2 as a C1 source. As a result, we herein report a transition-metal-free, base-catalyzed route for the efficient synthesis of formamides from CO_2 and amines using PMHS under mild reaction conditions (Scheme 1).

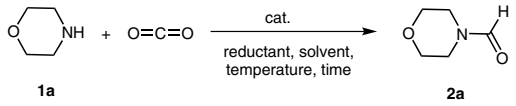
Table 1 demonstrates the effect of reaction parameters for the formylation of morpholine **1a** using CO_2 and PMHS as a model reaction. Initially, the reaction was carried out in the absence of catalyst, but the desired product was not obtained (Table 1, entry 1). Then, a series of experiments was



Scheme 1 Scope of formamide derivatives from amines, CO_2 and PMHS

performed to examine the reaction parameters such as nature of the catalyst, CO_2 pressure, temperature, reaction time, effect of PMHS loading and solvent to optimize the synthesis of the desired product **2a** from morpholine.

Table 1 Study of Reaction Parameters for Formylation of Morpholine Using CO_2 and PMHS[a]



Entry	Morpholine/PMHS (mmol:mmol)	Catalyst	CO_2 (MPa)	Temp (°C)	Time (h)	Yield of **2a** (%)[b]
1	1:4	–	3	100	12	NR
2	1:4	Cs_2CO_3	3	100	12	99[c]
3	1:4	Na_2CO_3	3	100	12	85
4	1:4	K_2CO_3	3	100	12	99[c]
5	1:4	K_2CO_3	–	100	24	NR
6[d]	1:4	K_2CO_3	3	100	12	42
7[e]	1:4	K_2CO_3	3	100	12	76
8[f]	1:4	K_2CO_3	3	100	12	39
9	1:4	K_2CO_3	2	100	12	68
10	1:4	K_2CO_3	4	100	12	99
11	1:4	K_2CO_3	3	120	12	99
12	1:4	K_2CO_3	3	80	12	65
13	1:4	K_2CO_3	3	100	16	99
14	1:4	K_2CO_3	3	100	8	69
15	1:6	K_2CO_3	3	100	12	98
16	1:2	K_2CO_3	3	100	12	50

[a] Reaction conditions: morpholine (1 mmol), catalyst (10.0 mol%), THF (5.0 mL), 100 °C, 12 h.
[b] Based on GC/GC–MS analysis. The yield was quantified by the external standard method using morpholine-1-carbaldehyde.
[c] Isolated yield after column chromatography purification. NR: no reaction.
[d] The reaction was performed neat.
[e] Solvent used was 1,4-dioxane.
[f] Solvent used was glycerol.

For the initial studies, the effect of catalysts such as Cs_2CO_3, Na_2CO_3 and K_2CO_3 was investigated (Table 1, entries 2–4). We observed that both Cs_2CO_3 and K_2CO_3 provided an excellent yield (99%) of the desired product (Table 1, entries 2 and 4) and so the less expensive K_2CO_3 was chosen as the best catalyst for the title reaction.

Reaction occurred under solvent-free conditions, but provided a very low yield of the desired product (Table 1, entry 6), whereas 1,4-dioxane and THF were found to afford good to excellent (76–99%) yields of **2a** (Table 1, entries 4 and 8). The effect of CO_2 pressure on the yield of the desired product was examined at 100 °C for 12 hours. The yield of **2a** increased to quantitative at 3 MPa (Table 1, entries 4, 9 and 10).

We investigated the effect of temperature on the yield of **2a** using K_2CO_3 as catalyst at 3 MPa CO_2 pressure ranging from 80 °C to 120 °C with a reaction time of 12 hours (Table 1, entries 4, 11 and 12). It was observed that, at 80 °C, the yield of **2a** was quite low (Table 1, entry 12). On increasing the reaction temperature from 100 °C to 120 °C the desired product was obtained in an excellent yield (99%) within 12 hours (Table 1, entry 11).

We studied the effect of reaction time, ranging from 8 hours to 16 hours (Table 1, entries 13 and 14). The maximum yield (99%) was obtained within 12 hours at 3 MPa pressure.

Finally, we focused on the amount of the PMHS (Table 1, entries 4, 15 and 16) and it was found that 1 mmol of morpholine and 4 mmol of PMHS provided the highest yield of the desired product (Table 1, entry 4). Accordingly, the optimized reaction conditions were: amine (1 mmol), K_2CO_3 as catalyst (10.0 mol%), THF as solvent (5.0 mL), PMHS (4.0 mmol), CO_2 pressure of 3 MPa, temperature of 100 °C and a reaction time of 12 hours.[20]

To check the generality of these reaction conditions, we examined the optimized protocol for N-formylation of a range of primary and secondary aliphatic and aromatic amines **1a–z**.

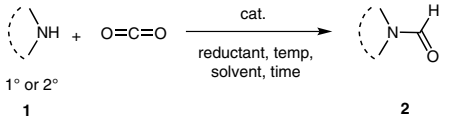
The N-formylation of aliphatic secondary amines **1b–f**, provided good yields (75–92%) of the corresponding desired products **2b–f** (Table 2, entries 2–6). It was observed that the bulkier aliphatic secondary amines provided moderate yields of the desired products, maybe due to steric hindrance (Table 2, entry 5). Substrate **1g** furnished selectively the N-formylation product **2g** in 54% yield without reduction of the double bond (Table 2, entry 7). Cyclic secondary amines gave the corresponding N-formylation products in a good to excellent yields (Table 2, entries 8, 9, 11–14). Unfortunately, the reaction did not proceed in the case of **1j** (Table 2, entry 10), presumably because of the sterically hindered and deactivating COOH group on the adjacent carbon atom of the amine. Furthermore, a second formylation of **1n** did not occur at the hindered site, with only monoformylation product **1n** being isolated in 85% yield (Table 2, entry 14).

The indoline substrate **1o** underwent efficient conversion to **2o** (78%; Table 2, entry 15), whereas 1,2,3,4-tetrahydroquinoline provided only trace amounts of product **1p** (Table 2, entry 16). The benzylic secondary amines **1q** and **1r** proved to react well, providing excellent yields (95% and 91%) of the desired formamides after 12 hours at 100 °C un-

der the optimized reaction conditions (Table 2, entries 17 and 18). The *N*-benzyl-2-methylpropan-2-amine (**1t**), possessing the *N*-*tert*-butyl group, was not converted into the corresponding product (**2t**; Table 2, entry 20). The aromatic secondary amine, *N*-methylaniline readily provided the desired product in good yield (93%; Table 2, entry 19), but *N*-methyl-2-nitroaniline (**1u**) did not provide the desired product, presumably due to steric reasons (Table 2, entry 21). Cyclohexylamine and aniline furnished the desired products in a moderate to good yields (Table 2, entries 22 and 23). However, anilines bearing *ortho* substituents (**1x**, **1x′** and **1x″**) did not give the corresponding formamide products (Table 2, entry 24). Reaction of [1,1′-biphenyl]-4-amine and *tert*-butylamine afforded the corresponding desired products **2y** and **2z** in moderate to good yields (59% and 70%; Table 2, entries 25 and 26).

In summary, herein we have reported the first example of the use of K_2CO_3 as an efficient catalyst for the formylation of amines by hydrosilylation of CO_2 using PMHS. We believe this system will add to the methodology for the synthesis of formamides.

Table 2 Synthesis of Formamides[a]



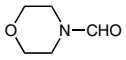
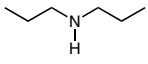
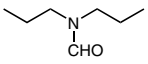
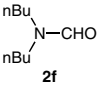
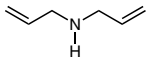
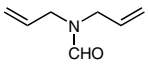
Entry	Substrate	Product	Yield (%)[b]
1	 **1a**	 **2a**	99[c]
2	 **1b**	 **1b**	92[c]
3	 **1c**	 **2c**	89[c]
4	 **1d**	 **2d**	87
5	 **1e**	 **2e**	51
6	 **1f**	 **2f**	75[c]
7	 **1g**	 **2g**	54

Table 2 (continued)

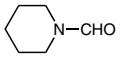
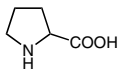
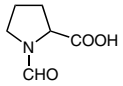
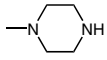
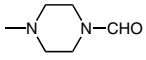
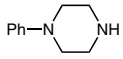
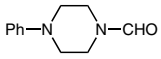
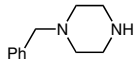
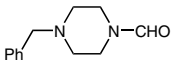
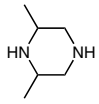
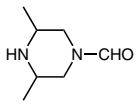
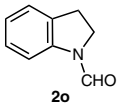
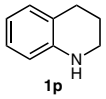
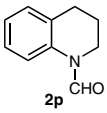
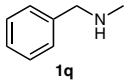
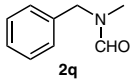
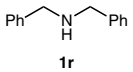
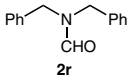
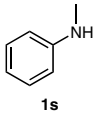
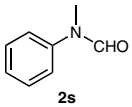
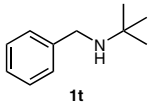
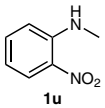
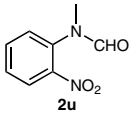
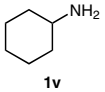
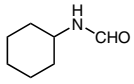
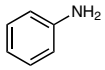
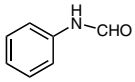
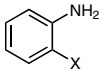
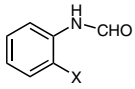
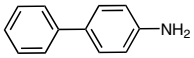
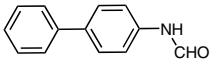
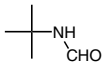
Entry	Substrate	Product	Yield (%)[b]
8	 **1h**	 **2h**	98
9	 **1i**	 **2i**	92
10	 **1j**	 **2j**	NR
11	 **1k**	 **2k**	88
12	 **1l**	 **2l**	84
13	 **1m**	 **2m**	71
14	 **1n**	 **2n**	85
15	 **1o**	 **2o**	78[c]
16	 **1p**	 **2p**	trace
17	 **1q**	 **2q**	95[c]
18	 **1r**	 **2r**	91
19	 **1s**	 **2s**	93[c]
20	 **1t**	**2t**	NR

Table 2 (continued)

Entry	Substrate	Product	Yield (%)[b]
21	 **1u**	 **2u**	NR
22	 **1v**	 **2v**	82[c]
23	 **1w**	 **2w**	85[c]
24	 X= F (**1x**), Cl (**1x'**), Br (**1x''**)	 X= F (**2x**), Cl (**2x'**), Br (**2x''**)	NR
25	 **1y**	 **2y**	59
26	 **1z**	 **2z**	70[c]

[a] Reaction conditions: substrate (1.0 mmol), anhyd K_2CO_3 (10.0 mol%), THF (5.0 mL), CO_2 (3 MPa), PMHS (4.0 mmol), 100 °C, 12 h. NR: no reaction.
[b] Based on GC/GC–MS analysis. The yield was quantified by using the external standard method using morpholine-1-carbaldehyde.
[c] Isolated yield after column chromatography purification.

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Supporting Information

Supporting information for this article is available online at http://dx.doi.org/10.1055/s-0035-1561571.

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(20) **General Procedure for the Synthesis of Formamide Derivatives**: The catalyst (10.0 mol%) was introduced into a 100-mL autoclave equipped with an overhead stirrer and an automatic temperature control system[5i] containing amine (1 mmol), PMHS (4.0 mmol) and THF (5.0 mL) at r.t. After sealing and flushing the reactor three times with 10 atm of N_2, followed by the CO_2 to the desired pressure, the reactor was heated and stirred vigorously at 530–600 rpm for 12 h. After completion of the reaction, the reactor was cooled to r.t. and the pressure was carefully released. Basic hydrolysis of the reaction mixture was carried out as previously described.[5h] The reaction mixture was then extracted with EtOAc (3 × 10 mL), the combined organic layers were dried over anhyd Na_2SO_4, filtered and evaporated in vacuo. The isolated crude oil product was further purified by column chromatography on 100–200 mesh size silica gel (elution with 20:4 → 10:2 petroleum ether–EtOAc) to provide the corresponding pure compound. The spectroscopic data are consistent with those reported in the literature and in agreement with the assigned structures.[21]
Morpholine-4-carbaldehyde (2a): colorless oil; yield: 99%. ^{1}H NMR (400 MHz, 30 °C, $CDCl_3$, TMS): δ = 7.92 (s, 1 H), 3.58–3.52 (m, 4 H), 3.44 (t, J = 4.0 Hz, 2 H), 3.28 (t, J = 4.0 Hz, 2 H). ^{13}C NMR (100 MHz, 30 °C, $CDCl_3$, TMS): δ = 160.81, 67.08, 66.26, 45.67, 40.44. GC–MS (EI): m/z (%) = 115 (100) [M]$^+$.
Indoline-1-carbaldehyde (2o): brown solid; yield: 78%. ^{1}H NMR (400 MHz, 30 °C, $CDCl_3$, TMS): δ (mixture of rotamers) = 8.92 (s, 1 H, major), 8.50 (s, 1 H, minor), 7.24–7.14 (m, 3 H), 7.05–7.01 (m, 1 H), 4.05 (t, J = 8.0 Hz, 2 H), 3.14 (t, J = 8.0 Hz, 2 H). ^{13}C NMR (100 MHz, 30 °C, $CDCl_3$, TMS): δ = 157.58, 140.93, 127.57, 126.06, 125.13, 124.28, 109.38, 44.64, 27.17. GC–MS (EI): m/z (%) = 147 (65) [M]$^+$.
***N*-Benzyl-*N*-methylformamide (2q)**: colorless oil; yield: 95%. ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C, TMS): δ (mixture of rotamers) = 8.26 (s, 1 H, major), 8.13 (s, 1 H, minor), 7.37–7.17 (m, 5 H), 4.50 (s, 2 H, minor), 4.37 (s, 2 H, major), 2.82 (s, 3 H, minor), 2.76 (s, 3 H, major). ^{13}C NMR (100 MHz, 30 °C, $CDCl_3$, TMS): δ (mixture of rotamers) = 162.74 (major), 162.57 (minor), 135.96 (minor), 135.69 (major), 128.88 (major), 128.67 (minor), 128.21 (major), 128.08 (minor), 127.62 (minor), 127.36 (major), 53.47 (major), 47.74 (minor), 34.05 (major), 29.44 (minor). GC–MS (EI): m/z (%) = 149 (100) [M]$^+$.
***N*-Methyl-*N*-phenylformamide (2s)**: brownish oil; yield: 93%. ^{1}H NMR (400 MHz, 30 °C, $CDCl_3$, TMS): δ = 8.39 (s, 1 H), 7.33 (t, J = 8.0 Hz, 2 H), 7.20 (t, J = 8.0 Hz, 1 H), 7.10 (d, J = 4.0 Hz, 2 H), 3.24 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$, 30 °C, TMS): δ (mixture of rotamers) = 162.27 (major), 162.17 (minor), 142.08, 129.55, 128.96, 126.32 (major), 126.16 (minor), 123.53, 122.26, 31.95. GC–MS (EI): m/z (%) = 135 (85) [M]$^+$.
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