Tetrahedron 66 (2010) 4479–4483

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

High-yielding synthesis of Weinreb amides via homogeneous catalytic carbonylation of iodoalkenes and iodoarenes

Attila Takács, Andrea Petz, László Kollár *

Department of Inorganic Chemistry, University of Pécs, H-7624 Pécs, PO Box 266, Hungary

ARTICLE INFO

Article history:
Received 27 January 2010
Received in revised form 13 April 2010
Accepted 19 April 2010
Available online 24 April 2010

Keywords:
Aminocarbonylation
Carbon monoxide
Weinreb amide
Palladium
Iodoalkene

ABSTRACT

Iodoarenes (iodobenzene and 2-iodothiophene) and iodoalkenes (1-iodocyclohexene, 1-iodo-4-*tert*-butylcyclohexene, 1-iodo-2-methylcyclohexene and 1-iodo-1-(1-naphthyl)ethene) were used as substrates in palladium-catalysed aminocarbonylation with *N*,*O*-dimethylhydroxylamine. The corresponding Weinreb amides were prepared in high isolated yields (up to 87%) when forcing conditions (40–60 bar of CO, 50 °C) were used. The aminocarbonylation provides the Weinreb amides as pure products in a chemoselective reaction. No formation of ketocarboxamides, due to double CO insertion, except for 2-iodothiophene, was observed even at 60 bar of CO pressure.

1. Introduction

Weinreb amides (*N*-methoxy-*N*-methyl amides), easily available from the corresponding acids or esters, represent an important family of acylating agents.[1] Their synthetic utility is due to the facile reaction with various organometallic reagents providing building blocks of versatile structure.[2] Their two major synthetic features, that is, the excellent acylating agent property towards organolithium or organomagnesium reagents and the synthetic equivalency for an aldehyde group has been reviewed recently.[3]

A great variety of amides are available via palladium-catalysed aminocarbonylation. The synthetic applicability of these catalytic reactions is due to the ease in structural variation of amides both on the amide nitrogen and on the carboxylic acid moieties. That is, instead of the conventional carboxylic acid—acyl chloride—amide route a direct carbonylation of haloaromatics or haloalkenes (preferably iodo derivatives) as well as those of the corresponding triflate surrogates can be used.[4–7] It is worth mentioning that aminocarbonylation has shown high tolerancy towards both the structure of the primary and secondary amine and that of the organic halide derivative. The efficacy of these reactions can also be demonstrated both by the synthesis of the great variety of simple model compounds and by the functionalization of biologically important skeletons.[7] This methodology has been used also in our laboratory as a powerful tool for the functionalization of the tropene[8] and steroidal skeletons.[9,10]

Although several straightforward synthetic methods, such as conversion of acid chlorides,[11,12] esters[13,14] and carboxylic acids[15] towards Weinreb amides are known, only sporadic results on their facile homogeneous catalytic synthesis, based on the use of simple building blocks, have been reported.[16–18] Recently, a general palladium-catalysed carbonylation for the conversion of aryl bromides to benzamide-type Weinreb amides[17] and that of the lactam-, lactone- and thiolactone-derived triflates into the corresponding heterocyclic Weinreb amides have been published.[18] To the best of our knowledge, they have been the only examples involving the application of *N*,*O*-dimethylhydroxylamine in catalytic aminocarbonylation. Due to the reduced reactivity of this *N*-nucleophile, from the variety of bidentate ligands tested, the application of a diphosphine with rigid structure and a large bite angle (Xantphos) was necessary to achieve yields of practical interest.[17]

Guided by our earlier experience that iodoalkenes and iodoarenes can smoothly be converted to the corresponding amides by using even hindered secondary amines and functionalised amines such as amino acid esters, we decided to investigate the catalytic synthesis of Weinreb amides based on the application of iodo derivatives as substrates and *N*,*O*-dimethylhydroxylamine as *N*-nucleophile. Accordingly, a clean and quantitative synthetic methodology is reported here for the direct synthesis of aryl and α,β-unsaturated *N*-methoxy-*N*-methyl amides (i.e., aryl and unsaturated Weinreb amides).

* Corresponding author. E-mail address: kollar@ttk.pte.hu (L. Kollár).

0040-4020/$ – see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2010.04.076

2. Results and discussion

The iodoaromatics (iodobenzene, **1** and 2-iodothiophene, **2**) and iodoalkenes (1-iodocyclohexene, **3**, 1-iodo-4-*tert*-butylcyclohexene, **4**, 1-iodo-2-methylcyclohexene, **5** and 1-iodo-1-(1-naphthyl) ethene, **6**) were reacted with *N*,*O*-dimethylhydroxylamine at 1 bar of CO in the presence of in situ generated palladium(0)-triphenylphosphine catalysts (Scheme 1). The palladium(0) complexes, able to activate both iodoarenes and iodoalkenes, were prepared in situ from palladium(II) acetate as described previously in detail.[19,20]

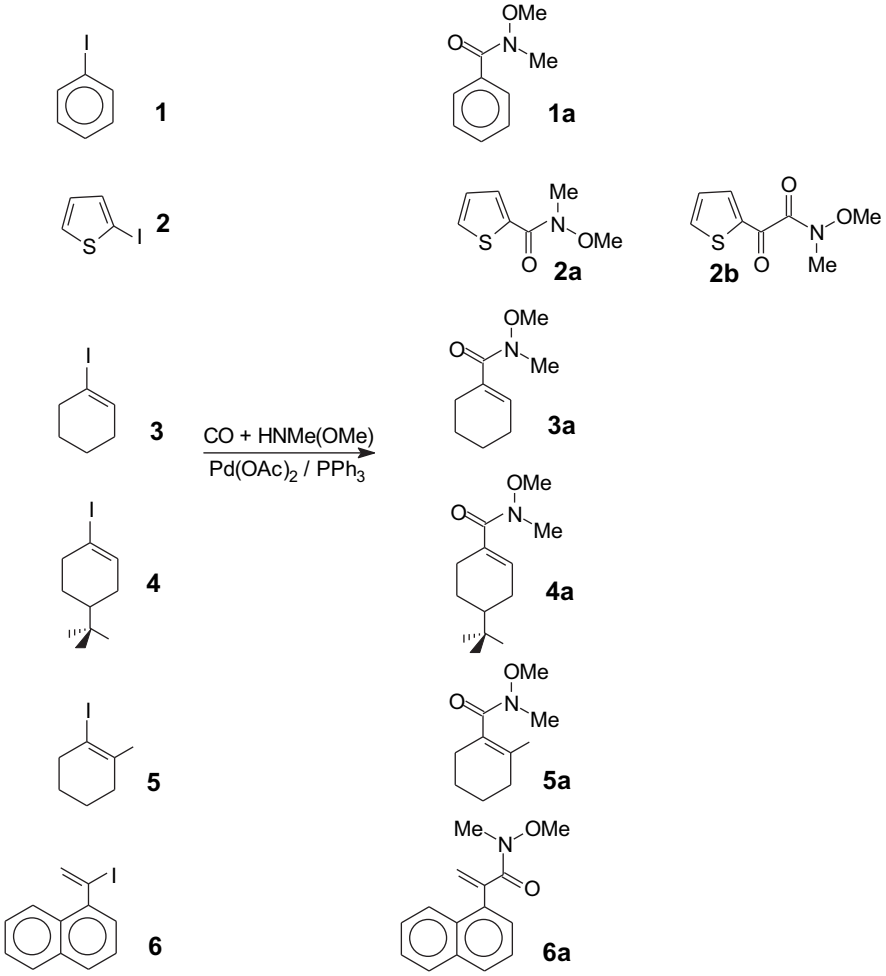
All the iodoaromatics and iodoalkenes above have shown lower reactivity towards *N*,*O*-dimethylhydroxylamine than towards the generally used primary and secondary amines as *N*-nucleophiles.[7] No reaction was observed with iodoaromatics at atmospheric CO pressure. In order to achieve higher (practically complete) conversion in a reasonable reaction time, higher CO pressure (60 bar) was necessary. Interestingly, while the aminocarbonylation of iodobenzene (**1**) is highly chemoselective yielding the expected Weinreb amide (**1a**) only, the application of 2-iodothiophene (**2**) as substrate resulted in the formation of both expected products, the corresponding amide (**2a**) and ketoamide (**2b**) due to simple and double CO insertion, respectively. It has to be added that **2b** was formed as a minor product (up to 8%) under all reaction conditions used.

Contrary to iodoarenes, iodoalkenes (**3**–**5**) react even at atmospheric CO pressure with conversion of 60%, 20% and 25%, respectively (Table 1). The 1-iodo-1-aryl-ethene type substrate (**6**) is featured by the highest reactivity among iodoalkenes also towards *N*,*O*-dimethylhydroxylamine, as observed previously in conventional palladium-catalysed aminocarbonylations.[21] The increase in the CO pressure resulted in practically complete conversions towards the expected Weinreb amides (**3a**–**6a**). The reaction is

Table 1
Palladium-catalysed aminocarbonylation of **1**–**6** and **10** with *N*,*O*-dimethylhydroxylamine as *N*-nucleophile[a]

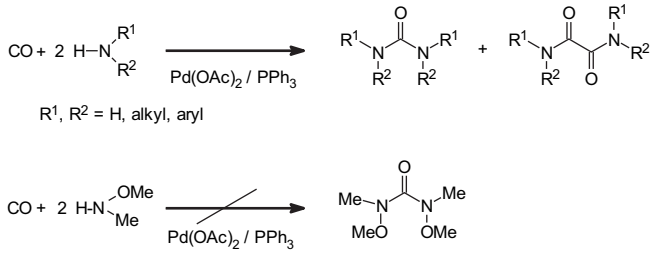
Entry	Subst.	p(CO) [bar]	R. time [h]	Conv.[b] [%]	Isolated yield[c] (amide) [%]
1	**1**	1	20	0	—
2	**1**	60	20	95	82 (**1a**)
3	**2**	1	20	0	—
4	**2**	60	110	>98	67 (**2a**), n.d.[d] (**2b**)
5	**3**	1	20	60	48 (**3a**)
6	**3**	40	85	>98	77 (**3a**)
7	**4**	1	20	20	n.d. (**4a**)
8	**4**	40	20	>98	87 (**4a**)
9	**5**	1	20	25	n.d. (**5a**)
10	**5**	60	72	>98	85 (**5a**)
11	**6**	1	20	>98	83 (**6a**)
12	**6**	60	20	>98	86 (**6a**)
13	**10**	60	72	>98	n.d. (**11**); 55 (**12**)

[a] Reaction conditions: 0.025 mmol $Pd(OAc)_2$; 0.05 mmol PPh_3, 1 mmol substrate (**1**–**6**, **10**); 1.1 mmol *N*,*O*-dimethylhydroxylamine hydrochloride; 10 mL DMF.
[b] Determined by GC/MS.
[c] Based on the amount of the substrate used (**1**–**6**, **10**).
[d] n.d.=not determined (i.e., the target compound was not isolated as a pure substance).



Scheme 1. Palladium-catalysed aminocarbonylation of iodoarenes (**1**,**2**) and iodoalkenes (**3**–**6**) with *N*,*O*-dimethylhydroxylamine.

completely chemoselective providing the expected *N*-methoxy-*N*-methyl carboxamide as the only product in all cases. It has been reported, that palladium(0)-catalysed aminocarbonylation is generally a highly selective reaction regarding the transformation of the wide variety of substrates (triflates or iodo derivatives).[4,7] However, the amine nucleophile, used commonly in excess, is carbonylated to *N*,*N*′-dialkyl- or *N*,*N*,*N*′,*N*′-tetraalkylurea derivatives (and, in less amount, to the corresponding glyoxylamides). During this study, the carbonylation of the *N*,*O*-dimethylhydroxylamine nucleophile did not take place (Scheme 2), so no nucleophile was lost in the form of a urea-type derivative and a more facile isolation technique could be used.



Scheme 2. Palladium-catalysed carbonylation of *N*-nucleophiles as a side-reaction.

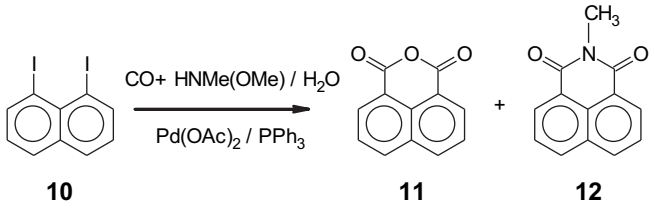
It is worth noting, that phosphine/palladium ratio as low as 2/1 has to be used. In this way, one equivalent of triphenylphosphine acts as a reducing agent in the reduction of palladium(II) to palladium(0) while it is oxidised to triphenylphoshine oxide. The other PPh_3 coordinates to Pd(0) resulting in coordinatively highly unsaturated reactive species.[19,20] In this way, an easy to handle, cheap, highly active palladium(0)-triphenylphosphine in situ system of synthetic interest was obtained.

Due to the highly polarizable iodo-substituent, conversions of practical interest have been achieved with all substrates. Furthermore, the application of iodoalkenes/iodoarenes as enol-triflate/aryltriflate surrogates leads to reaction mixtures, which could be worked-up by simple methods. Consequently, the Weinreb amides were isolated in high yields.

Compared the above results with those obtained previously with primary and secondary amines as *N*-nucleophiles,[21,22] it could be stated that *N*,*O*-dimethylhydroxylamine shows much lower reactivity. Therefore more severe reaction conditions had to be used. However, it has been revealed by detailed GC/MS analyses that in case of **6** high conversions have been obtained even after a short reaction time. The aminocarbonylation of this highly reactive substrate towards **6a** at atmospheric CO pressure resulted in 21%, 43%, 56%, 84%, 95% and 99% conversions in 15 min, 30 min, 1 h, 2 h, 3 h and 5 h, respectively. In this way, high conversions can be obtained in 20 h (Table 1), enabling the facile isolation of the exclusive amide product.

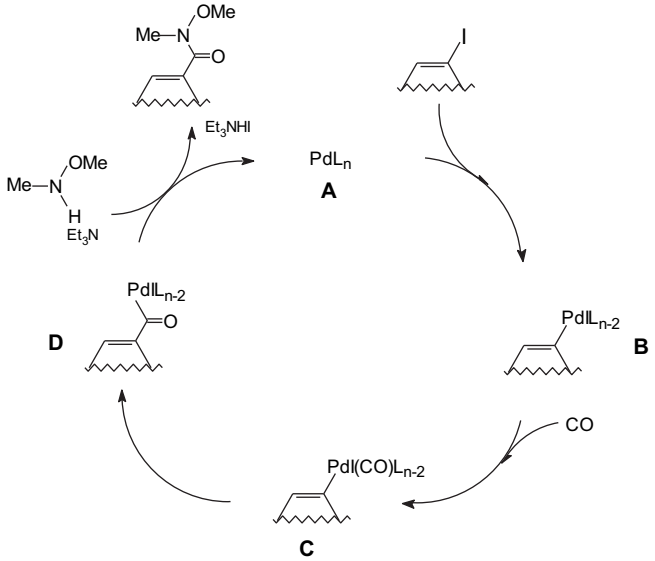
As for the limitations of the iodoaromatics-based catalytic synthesis of Weinreb amides, it should be added, that 2-iodopyridine (**7**) and its *ortho*-hydroxy-substituted derivative, 3-hydroxy-2-iodo-6-methylpyridine (**8**), as well as 2-iodo-imidazole (**9**) proved to be unreactive under the conditions used above. Neither the corresponding carboxamides, the only products in the aminocarbonylation of **7** with primary and secondary amines,[21] nor the ketocarboxamides were formed.

An unexpected reaction was observed with 1,8-diiodonaphthalene (**10**). The mixture of two products, that of *N*-methyl-1,8-naphthalimide (**12**) and naphthalene-1,8-dicarboxylic anhydride (**11**) was obtained in a ratio of ca. 80/20 (Scheme 3). The formation of **11** can be explained by the low reactivity of the nucleophile and the presence of traces of water in the solvent (and even the adsorbed water on the wall of the glass flask). It should be noted that the application of flame-dried apparatus decreased the amount of **11** drastically. The bis(palladium-acyl) intermediate, obtained from **10** by double oxidative addition followed by CO insertion, could form **11** by hydrolysis or **12** by reacting with *N*,*O*-dimethylhydroxylamine. To the best of our knowledge, the application of *N*,*O*-dimethylhydroxylamine as a methylamine source ('masked methylamine') in catalysis is unprecedented.



Scheme 3. The carbonylation reactions of 1,8-diiodonaphthalene.

A simplified reaction mechanism of the aminocarbonylation of an iodoalkene with *N*,*O*-dimethylhydroxylamine towards the corresponding Weinreb amide is shown on Scheme 4. The oxidative addition of the iodoalkene substrate on palladium(0) complex (**A**), formed in situ from palladium(II) acetate and PPh_3 (vide supra), takes place. The resulted palladium(II)-alkenyl intermediate (**B**) activates CO yielding the terminal carbonyl complex (**C**). The migratory insertion of CO into the palladium–alkenyl bond provides the acyl intermediate (**D**), which undergoes reductive elimination in the presence of a base (triethylamine) and *N*,*O*-dimethylhydroxylamine in the product-forming step, while the catalytically active, coordinatively unsaturated palladium(0) complex is re-formed.



Scheme 4. A simplified reaction mechanism for the aminocarbonylation of an iodoalkene with *N*,*O*-dimethylhydroxylamine.

3. Conclusion

We have found that various types of iodoalkenes and iodoaromatics show good reactivity in the palladium-catalysed aminocarbonylation using *N*,*O*-dimethylhydroxylamine as the *N*-nucleophile. A clean and quantitative catalytic synthetic methodology was developed for the direct synthesis of the corresponding *N*-methoxy-*N*-methyl amides, i.e., for that of aryl and unsaturated Weinreb amides. It is worthy of note that even the most simple and

easily available palladium-triphenylphosphine in situ catalyst proved to be active under relatively mild reaction conditions. In this way, a high-yielding, simple method for the synthesis of these widely used synthetic building blocks is provided.

4. Experimental

4.1. General procedures

^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Varian Inova 400 spectrometer at 400.13 MHz and 100.62 MHz, respectively. Chemical shifts δ are reported in parts per million relative to residual $CHCl_3$ (7.26 and 77.00 ppm for ^{1}H and ^{13}C, respectively). Elemental analyses were measured on a 1108 Carlo Erba apparatus. Samples of the catalytic reactions were analysed with a Hewlett Packard 5830A gas chromatograph fitted with a capillary column coated with OV-1.

The *N*,*O*-dimethylhydroxylamine and the iodoaromatics were purchased from Aldrich. The iodoalkenes (1-iodocyclohexene,[23] 1-iodo-4-*tert*-butylcyclohexene,[23] 1-iodo-2-methylcyclohexene[23] and 1-iodo-1-(1-naphthyl)ethane[22]) were synthesised as described before.

4.2. Aminocarbonylation experiments at normal pressure

In a typical experiment a solution of $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), PPh_3 (13.1 mg, 0.05 mmol), 1.0 mmol iodo substrate (**1**–**9**), 1.1 mmol *N*,*O*-dimethylhydroxylamine hydrochloride (107.3 mg, 1.1 mmol) were dissolved in 10 mL of DMF under argon. Triethylamine (0.5 mL) was added to the homogeneous yellow solution and the atmosphere was changed to CO. The colour changed to dark red. The reaction was conducted for the given reaction time at 50 °C. Some metallic palladium was formed at the end of the reaction, which was filtered off. A sample of this solution was immediately analysed by GC/MS. The mixture was then concentrated to dryness. The residue was dissolved in chloroform (20 mL) and washed with water (20 mL). The organic phase was thoroughly washed with 5% HCl (2×20 mL), saturated $NaHCO_3$ (20 mL), brine (20 mL), dried over Na_2SO_4 and concentrated to a yellow waxy material or a thick oil. Chromatography (silica, chloroform, then chloroform/ethyl acetate mixtures) afforded the desired compounds typically as pale brown viscous materials or yellow solids.

The synthesis of compounds **1a**,[14,15,24] **2a**,[25,26] **3a**[18] and **12**[27] by conventional methods have been previously reported. Our analytical data below are in good agreement with the reported values. Due to some minor differences in the analytical data (e.g., coupling constants) full characterization are given here also for these compounds.

4.3. Aminocarbonylation experiments at high pressure

A mixture of **1** (or **2**–**9**) (1 mmol), palladium(II) acetate (5.6 mg, 0.025 mmol) and PPh_3 (13.1 mg, 0.05 mmol) was dissolved in 10 mL of DMF under argon, and NEt_3 (0.5 mL) and *N*,*O*-dimethylhydroxylamine hydrochloride (107.3 mg, 1.1 mmol) as *N*-nucleophile was added. The reaction mixture was then transferred under argon into a 100 mL stainless steel autoclave, which was pressurized to 60 bar with CO and the magnetically stirred mixture was heated in an oil bath at 50 °C for the reaction time given in Table 1. The work-up procedure was identical with that given above.

4.4. Characterization of the amide and ester products

*4.4.1. N-Methyl-N-methoxy-benzamide (**1a**).* δ_H (400 MHz, $CDCl_3$) 7.66 (d, 8.0 Hz, 2H, Ph); 7.38–7.50 (m, 3H, Ph); 3.57 (s, 3H, OCH_3); 3.35 (s, 3H, NCH_3). δ_C (100.6 MHz, $CDCl_3$) 170.0; 134.2; 130.5; 128.1; 128.0; 61.0; 33.8. IR (KBr, (cm^{-1})): 1648 (CON). MS *m*/*z* (rel int. %): 165 (3), 105 (100), 77 (52), 51 (15). Anal. Calcd for $C_9H_{11}NO_2$ (165.19): C, 65.44; H, 6.71; N, 8.48; found: C, 65.32, H, 6.86; N, 8.23; R_f (10% EtOAc/$CHCl_3$) 0.63; pale yellow oil.

*4.4.2. N-Methyl-N-methoxy-thiophene-2-carboxamide (**2a**).* δ_H (400 MHz, $CDCl_3$) 7.95 (d, 3.7 Hz, 1H, Tioph); 7.55 (d, 4.9 Hz, 1H, Tioph); 7.12 (d, 3.7 Hz, 4.9 Hz, 1H, Tioph); 3.79 (s, 3H, OCH_3); 3.40 (s, 3H, NCH_3). δ_C (100.6 MHz, $CDCl_3$) 162.3; 135.8; 134.4; 132.2; 126.8; 61.5; 33.1. IR (KBr, (cm^{-1})): 1655 (CON). MS *m*/*z* (rel int. %): 171 (6), 111 (100), 83 (10), 57 (2). Anal. Calcd for $C_7H_9NO_2S$ (171.21): C, 49.11; H, 5.30; N, 8.18; found: C, 49.02, H, 5.45; N, 8.01; R_f (10% EtOAc/$CHCl_3$) 0.56; yellow oil.

*4.4.3. N-Methyl-N-methoxy-cyclohex-1-enecarboxamide (**3a**).* δ_H (400 MHz, $CDCl_3$) 6.14 (br s, 1H, =CH); 3.62 (s, 3H, OCH_3); 3.21 (s, 3H, NCH_3); 2.2–2.26 (m, 2H, CH_2); 2.08–2.14 (m, 2H, CH_2); 1.58–1.70 (m, 4H, 2×CH_2). δ_C (100.6 MHz, $CDCl_3$) 172.0; 133.9; 131.0; 61.0; 33.7; 25.6; 25.0; 22.2; 21.7. IR (KBr, (cm^{-1})): 1655 (CON); ca. 1620 (sh, C=C). MS *m*/*z* (rel int. %): 169 (2), 109 (100), 81 (70), 79 (45), 53 (16). Anal. Calcd for $C_9H_{15}NO_2$ (169.22): C, 63.88; H, 8.93; N, 8.28; found: C, 63.70, H, 8.85; N, 8.03; R_f (10% EtOAc/$CHCl_3$) 0.54; yellow oil.

*4.4.4. N-Methyl-N-methoxy-4-tert-butyl-cyclohex-1-enecarboxamide (**4a**).* δ_H (400 MHz, $CDCl_3$) 6.19–6.22 (m, 1H, =CH); 3.63 (s, 3H, OCH_3); 3.21 (s, 3H, NCH_3); 2.15–2.40 (m, 3H, CH^tBu+ =$CHCH_2$); 1.80–1.96 (m, 2H, CH_2); 1.10–1.35 (m, 2H, CH_2). δ_C (100.6 MHz, $CDCl_3$) 171.9; 133.6; 131.8; 61.0; 43.5; 33.7; 32.2, 27.2; 27.1, 26.9; 23.7. IR (KBr, (cm^{-1})): 1659 (CON); 1632 (C=C). MS *m*/*z* (rel int. %): 225 (2), 210 (4), 165 (100), 95 (20), 81 (31), 57 (38). Anal. Calcd for $C_{13}H_{23}NO_2$ (225.33): C, 69.29; H, 10.29; N, 6.22; found: C, 69.10, H, 10.45; N, 6.03; R_f (10% EtOAc/$CHCl_3$) 0.65; yellow oil.

*4.4.5. N-Methyl-N-methoxy-2-methyl-cyclohex-1-enecarboxamide (**5a**).* δ_H (400 MHz, $CDCl_3$) 3.63 (s, 3H, OCH_3); 3.21 (s, 3H, NCH_3); 1.25–2.20 (m, 8H, 4×CH_2); 1.62 (s, 3H, =CCH_3). δ_C (100.6 MHz, $CDCl_3$) 171.6; 139.1; 129.6; 60.9; 33.9; 30.9; 30.5; 30.0; 25.2; 20.0. IR (KBr, (cm^{-1})): 1641 (CON). MS *m*/*z* (rel int. %): 183 (2), 123 (100), 95 (61), 67 (33). Anal. Calcd for $C_{10}H_{17}NO_2$ (183.25): C, 65.54; H, 9.35; N, 7.64; found: C, 65.37, H, 9.51; N, 7.50; R_f (20% EtOAc/$CHCl_3$) 0.56; pale yellow oil.

*4.4.6. N-Methyl-N-methoxy-2-(1-naphthyl)acrylamide (**6a**).* δ_H (400 MHz, $CDCl_3$) 8.12 (d, 7.8 Hz, 1H, Naph); 7.77–7.85 (m, 2H, Naph); 7.40–7.51 (m, 5H, Naph); 6.11 (s, 1H, =CH); 5.65 (s, 1H, =CH); 3.10 (s, 3H, OCH_3); 2.93 (s, 3H, NCH_3). δ_C (100.6 MHz, $CDCl_3$) 171.3; 144.6; 136.2; 133.6; 131.1; 128.3; 128.2; 126.4; 125.9 (double intensity); 125.3; 125.2; 123.9; 60.3; 33.1. IR (KBr, (cm^{-1})): 1656 (CON). MS *m*/*z* (rel int. %): 241 (11), 181 (10), 153 (100), 76 (5). Anal. Calcd for $C_{15}H_{15}NO_2$ (241.29): C, 74.67; H, 6.27; N, 5.80; found: C, 74.50, H, 6.45; N, 5.66; R_f (10% EtOAc/$CHCl_3$) 0.75; yellow viscous material.

*4.4.7. N-Methyl-N-methoxy-thiophen-2-yl-glyoxylamide (**2b**).* δ_H (400 MHz, $CDCl_3$) 8.41 (d, 3.6 Hz, 1H, Tioph); 7.79 (d, 4.8 Hz, 1H, Tioph); 7.18 (dd, 3.6 Hz, 4.8 Hz, 1H, Tioph); 3.72 (s, 3H, OCH_3); 3.35 (s, 3H, NCH_3). δ_C (100.6 MHz, $CDCl_3$) 178.4; 166.4; 135.9; 135.8; 133.3; 128.5; 62.3; 31.7. MS *m*/*z* (rel int. %): 199 (1), 111 (100), 83 (10), 57 (5). Compound **2b** could not be isolated as pure compound. The above data were obtained from a mixture of **2a**/**2b**=3/1.

*4.4.8. N-Methyl-1,8-naphthalimide (**12**).* ^{1}H NMR($CDCl_3$) δ: 8.60 (d, 7.3 Hz, 2H, Naph); 8.21 (d, 8.3 Hz, 2H; Naph); 7.77 (dd, 7.3 Hz, 8.3 Hz, 2H, Naph); 3.57 (s, 3H, NCH_3). ^{13}C NMR ($CDCl_3$) δ: 163.1; 133.9; 132.5;

132.0; 129.8; 125.5; 121.1; 37.2. IR (KBr, (cm^{-1})): 1771, 1736 (OCNCO). MS *m*/*z* (rel int. %): 211 (60), 198 (24), 183 (12), 167 (93), 166 (100), 154 (49), 139 (17), 126 (73). Anal. Calcd. for $C_{13}H_9NO_2$ (211.22): C, 73.92; H, 4.29; N, 6.63; found: C, 73.74; H, 4.49; N, 6.40; R_f (10% EtOAc/$CHCl_3$) 0.73; white solid, mp 200–201 °C.

Acknowledgements

The authors thank the Hungarian Research Fund (OTKA CK78553), the Joint Project of the European Union—Hungarian National Development Program (GVOP-3.2.1-2004-04-0168/3) and Science, Please! Research Team on Innovation (SROP-4.2.2./08/1/2008-0011) for the financial support and Johnson Matthey for the generous gift of palladium(II) acetate.

References and notes

1. Khlestkin, V. K.; Mazhukin, D. G. *Curr. Org. Chem.* **2003**, *7*, 967–993 and references cited therein.
2. Sha, C.-K.; Huang, S.-J.; Zhan, Z.-P. *J. Org. Chem.* **2002**, *67*, 831–836.
3. Balasubramaniam, S.; Aidhen, I. S. *Synthesis* **2008**, 3707–3738 and references cited therein.
4. Skoda-Földes, R.; Kollár, L. *Curr. Org. Chem.* **2002**, *6*, 1097–1119.
5. *Applied Homogeneous Catalysis with Organometallic Compounds*; Cornils, B., Herrmann, W. A., Eds.; Wiley-VCH: Weinheim, 1996; *Transition Metals for Organic Synthesis*; Beller, M., Bolm, C., Eds.; Wiley-VCH: Weinheim, 1998; Vol. I–II.
6. Colquhoun, H. M.; Thompson, D. J.; Twigg, M. V. *Carbonylation. Direct Synthesis of Carbonyl Compounds*; Plenum: New York, NY and London, 1991.
7. Arcadi, A. Carbonylation of Enolizable Ketones (Enol Triflates) and Iodoalkenes In *Modern Carbonylation Methods*; Kollár, L., Ed.; Wiley-VCH: Weinheim, 2008; Chapter 9, pp 223–250.
8. Horváth, L.; Berente, Z.; Kollár, L. *Lett. Org. Chem.* **2007**, *4*, 236–238.
9. Balogh, J.; Mahó, S.; Háda, V.; Kollár, L.; Skoda-Földes, R. *Synthesis* **2008**, 3040–3042.
10. Ács, P.; Takács, A.; Szilágyi, A.; Wölfling, J.; Schneider, G.; Kollár, L. *Steroids* **2009**, *74*, 419–423 and references cited therein.
11. Nahm, S.; Weinreb, S. M. *Tetrahedron Lett.* **1981**, *22*, 3815–3818.
12. Sibi, M. P. *Org. Prep. Proced. Int.* **1993**, *25*, 15–42.
13. Colobert, F. C.; des Mazery, R.; Solladier, G.; Carreño, M. C. *Org. Lett.* **2002**, *4*, 1723–1725.
14. Williams, J. M.; Jobson, R. B.; Yasuda, N.; Marchesini, G.; Dolling, U.-H.; Grabowski, E. J. J. *Tetrahedron Lett.* **1995**, *36*, 5461–5464.
15. Woo, J. C. S.; Fenster, E.; Dake, G. R. *J. Org. Chem.* **2004**, *69*, 8984–8986 and references cited therein.
16. Murakami, M.; Hoshino, Y.; Yto, H.; Yto, Y. *Chem. Lett.* **1998**, 163–164.
17. Martinelli, J. R.; Freckmann, D. M. M.; Buchwald, S. L. *Org. Lett.* **2006**, *8*, 4843–4846.
18. Deagostino, A.; Larini, P.; Occhiato, E. G.; Pizzuto, L.; Prandi, C.; Venturello, P. *J. Org. Chem.* **2008**, *73*, 1941–1945.
19. Amatore, C.; Carre, E.; Jutand, A.; M'Barki, M. A.; Meyer, G. *Organometallics* **1995**, *14*, 5605–5614 and references cited therein.
20. Csákai, Z.; Skoda-Földes, R.; Kollár, L. *Inorg. Chim. Acta* **1999**, *286*, 93–97.
21. Takács, A.; Jakab, B.; Petz, A.; Kollár, L. *Tetrahedron* **2007**, *63*, 10372–10378.
22. Takács, A.; Farkas, R.; Petz, A.; Kollár, L. *Tetrahedron* **2009**, *65*, 4795–4800.
23. Müller, E.; Péczely, G.; Skoda-Földes, R.; Takács, E.; Kokotos, G.; Bellis, E.; Kollár, L. *Tetrahedron* **2005**, *61*, 797–802 and references cited therein.
24. Dineen, T. A.; Zajac, M. A.; Myers, A. G. *J. Am. Chem. Soc.* **2006**, *126*, 16406–16409.
25. Tunoori, A. R.; White, J. M.; Georg, G. I. *Org. Lett.* **2000**, *2*, 4091–4093.
26. White, J. M.; Tunoori, A. R.; Turunen, B. J.; Georg, G. I. *J. Org. Chem.* **2004**, *69*, 2573–2576.
27. Somich, C.; Mazzocchi, P. H.; Ammon, H. L. *J. Org. Chem.* **1987**, *52*, 3614–3619.