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Yu-Chao Yuan, Raghu Kamaraj, Christian Bruneau, Thierry Labasque, Thierry Roisnel, et al.. Unmasking Amides: Ruthenium-Catalyzed Protodecarbonylation of N-Substituted Phthalimide Derivatives. *Organic Letters*, 2017, 19 (23), pp.6404-6407. 10.1021/acs.orglett.7b03278 . insu-01639565

HAL Id: insu-01639565

<https://insu.hal.science/insu-01639565>

Submitted on 3 May 2018

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Unmasking Amides: Ruthenium-Catalyzed Protodecarbonylation of *N*-Substituted Phthalimide Derivatives

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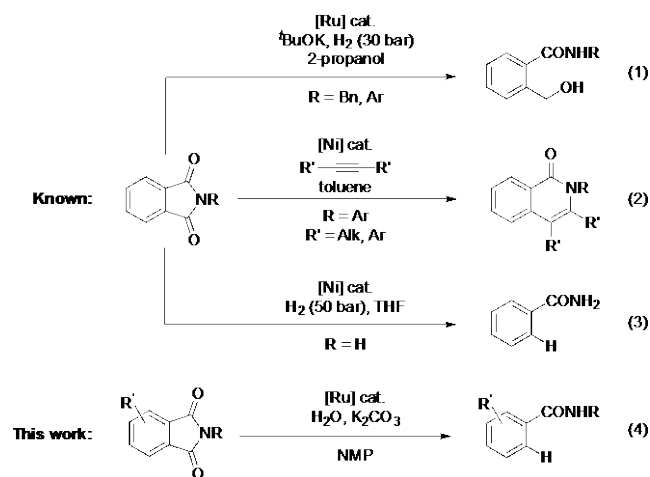
Supporting Information

ABSTRACT: The unprecedented transformation of a wide range of synthetically appealing phthalimides into amides in a single step operation has been achieved in high yields and short reaction times using a ruthenium catalyst. Mechanistic studies revealed a unique, homogeneous pathway involving five-membered ring opening and CO₂ release with water being the source of protons.

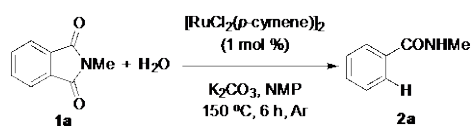
The phthalimide motif remains amongst the most widely used functional group in chemical synthesis. It enables the protection of primary amines and also, it behaves as an excellent nucleophile to install primary amines at will after treatment with hydrazine.¹ Phthalimides have also been applied as dyes,² porous solids,³ polymers,⁴ organocatalysts,⁵ and for different biological applications.⁶ In the last decades, phthalimides have also been conceived as key building blocks leading to important chemical skeletons due to their unique molecular structure. They are traditionally reduced employing over-stoichiometric amounts of strong reagents (LiAlH₄⁷ or BH₃⁸), superacids⁹ or metal salts derived from Al,¹⁰ Sn¹¹ and Zn¹² under harsh reaction conditions. From a sustainable point of view, homogeneous catalysis has been considered to account for the functionalization of phthalimides under milder reaction conditions. As such, pharmaceutically- and agrochemically-relevant heterocyclic compounds have been obtained starting from phthalimides *via* (i) transition metal-catalyzed hydrogenations,¹³ (ii) fluoride- and zinc-catalyzed reductions with silanes¹⁴ and (iii) ruthenium- and cobalt-catalyzed reductive alkoxylation and amination.¹⁵ In all the above-stated approaches the bicyclic structure of the phthalimide skeleton remained unreacted after selective hydrogen or nucleophile incorporation.¹³⁻¹⁵

On the other hand, examples leading to the selective cleavage of the phthalimide skeleton are extremely rare, which highlights the challenges associated with these types of transformations.¹⁶ For instance, in 2007, a ruthenium catalyst was reported to hydrogenate *N*-protected phthalimides, leading to valuable alcohol-amide products in the presence of ^tBuOK as

strong base and 30 bar of H₂ (eq 1).^{16a} One year later, a nickel catalyst enabled the decarbonylative addition of *N*-arylphthalimides to alkynes, providing isoquinolones (eq 2).^{16b} Finally, in 2013, a nickel catalyst was reported to hydrogenate phthalimide to benzamide (one example) in 82% selectivity under 50 bar of H₂ after 72 h of reaction time (eq 3).^{16c} Clearly, the possibilities in terms of molecular diversity arising from breaking the phthalimide backbone in a controlled manner and milder reaction conditions are under-developed, especially, considering that they could lead to new shortcuts in multi-step chemical synthesis. Herein, we present a general and efficient ruthenium-catalyzed protocol enabling the highly chemoselective protodecarbonylation of *N*-substituted phthalimide derivatives into amides as well as preliminary mechanistic studies that suggest an unexpected decarboxylation pathway (eq 4). It is relevant to highlight that amides are ubiquitous building blocks in the fine and bulk chemical industry, and disclosing new pathways towards their synthesis is always appealing.¹⁷



Based on previous contributions dealing with the formation of phthalimides from amides *via* ruthenium catalysis and the reversibility of some of the steps claimed in the catalytic cycle,¹⁸ we embarked on the study of the opposite reaction (Table 1). After screening of suitable reaction conditions

Table 1. Optimization of Reaction Conditions^a

entry	deviation from standard conditions	2a (%) ^b
1	none	>99 (93) ^c
2	with 0.5 mol % of [RuCl ₂ (<i>p</i> -cymene)] ₂	74
3	130 °C instead of 150 °C	69
4	110 °C instead of 150 °C	0
5	no [RuCl ₂ (<i>p</i> -cymene)] ₂	0
6	no K ₂ CO ₃	0
7	air instead of Argon	10
8	undistilled NMP	18
9	[RuCl ₃ ·xH ₂ O] instead of [RuCl ₂ (<i>p</i> -cymene)] ₂	35
10	[Ru ₃ (CO) ₁₂] instead of [RuCl ₂ (<i>p</i> -cymene)] ₂	traces
11	1 equivalent of K ₂ CO ₃	43
12	2 equivalents of K ₂ CO ₃	74
13	no H ₂ O and 24 h reaction time	56
14	with overnight-dried K ₂ CO ₃	50
15	H ₂ O instead of NMP	traces
16	with H ₂ (1 bar)	8

^a1a (0.4 mmol), H₂O (0.6 mmol), K₂CO₃ (1.2 mmol), [RuCl₂(*p*-cymene)]₂ (1 mol %) in NMP (2 mL) at 150 °C for 6 h under argon atmosphere.

^bYield estimated by ¹H NMR spectroscopy analysis using 1,3,5-trimethoxybenzene as internal standard. ^cIsolated yield.

(Table S1, Supporting Information), it was found that *N*-methylphthalimide (**1a**) was fully converted into the corresponding amide **2a** in 93% yield with [RuCl₂(*p*-cymene)]₂ as pre-catalyst (1 mol %), water (1.5 equiv) and K₂CO₃ (3 equiv) in *N*-methyl-2-pyrrolidone (NMP) at 150 °C after 6 h under inert atmosphere (Table 1, entry 1). The reaction was also efficient when being conducted at gram scale (97% yield, Figure S1). Decreasing the catalyst loading to 0.5 mol % led to 74% yield of **2a** (Table 1, entry 2). Lower reaction temperatures (130 °C and 110 °C) were detrimental for the catalysis (Table 1, entry 3-4). Control experiments indicated no conversion of **1a** without the ruthenium complex or the base as well as the need of argon atmosphere and distilled NMP (Table 1, entries 5-8). Other ruthenium complexes ([RuCl₃·xH₂O]) and [Ru₃(CO)₁₂] did not improve the system (Table 1, entries 9-10). The reaction was found to depend on the amount of K₂CO₃, with 43% and 74% conversion of **1a** obtained in the presence of one and two equivalents of K₂CO₃, respectively (Table 1, entries 11-12). The role of H₂O in the outcome of the reaction was evaluated too. Without adding water, 56% conversion of **1a** was observed after 24 h reaction time (Table 1, entry 13); the protons probably coming from traces of water in K₂CO₃ as evidenced by the drop in the conversion of **1a** (50%) when performing the catalysis with overnight-dried K₂CO₃ (Table 1, entry 14). Performing an experiment with a mixture of solvents NMP:D₂O (v/v 9:1) indicated full incorporation of deuterium at the aromatic carbon previously linked to the carbonyl moiety (**2a-d**); thus suggesting that water is the source of protons of the reaction (Figure 1a). The fast proton exchange during the work-up might explain the non-deuterated N-H amide group in **2a-d**. Unfortunately, using water as solvent inhibited the catalysis (Table 1, entry 15).

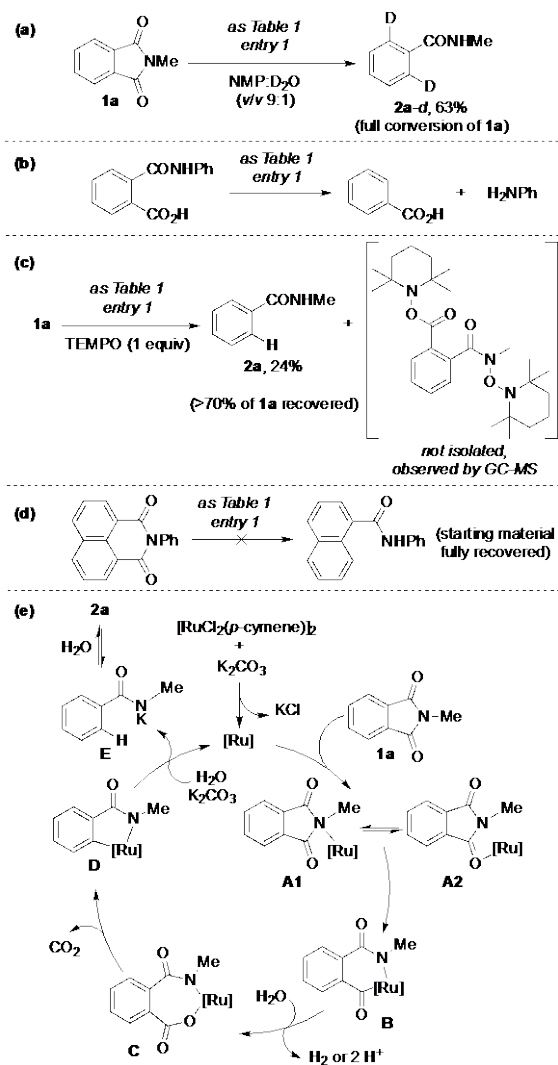


Figure 1. Mechanistic considerations. (a) Deuteration experiments. (b) Study on a plausible intermediate. (c) Trapping experiments. (d) Study on a substrate with a six-membered ring phthalimide. (e) A proposed catalytic cycle.

To gain further insights into the reaction mechanism, the gas phase of the reaction mixture was qualitatively analyzed by GC. It indicated the presence of H₂ and CO₂ as the major components (Figures S2-S4). The detection of H₂ together with the deuteration experiments might indicate the formation of ruthenium-hydride species during the catalytic cycle. However, the similar amounts of H₂ detected in a blank experiment and the fact that the catalytic reaction was almost unproductive under 1 bar of H₂ (Table 1, entry 16) preclude the involvement of H₂ in the catalytic cycle and ruled out a standard ruthenium-catalyzed hydrogenation mechanism.^{16a} Regarding the formation of CO₂, control experiments indicated that CO₂ was formed during the decarbonylation of the phthalimide ring since without the substrate almost no CO₂ was detected. To verify whether the reaction is initiated via hydrolysis of the phthalimide ring, 2-(phenylcarbamoyl)benzoic acid was submitted to the standard reaction conditions. Benzoic acid and aniline were the only products formed (Figure 1b), thereby excluding any hydrolysis of the phthalimide backbone previous to the decarboxylation process. In order to trap some potential intermediates, the catalysis was performed in the presence of 1 equivalent of TEMPO [TEMPO = (2,2,6,6-

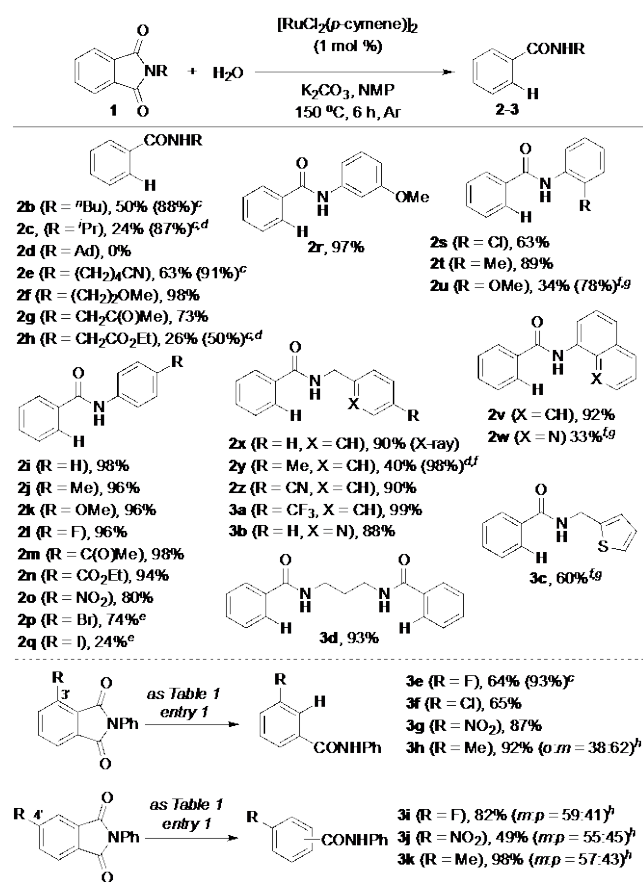
tetramethylpiperidin-1-yl)oxy]. Although the conversion of **1a** decreased to <30%, the formation of ring-opened intermediates containing two fragments of TEMPO ($m/z = 474$) were detected by GC-MS analysis (Figure 1c). In addition, performing the catalytic reaction with a phthalimide build-up on a six-membered ring did not proceed (Figure 1d), indicating that the ring strain release in **1a** is probably the driving force for the initial step of the catalytic cycle. Mercury tests indicated the homogeneous regime of the catalysis and attempts to identify ruthenium intermediates by different spectroscopic analysis failed so far.

Considering the above findings and previous contributions,^{18,19} a mechanism is tentatively postulated in Figure 1e. First, ruthenium chloride-free species were formed after reaction of $[\text{RuCl}_2(p\text{-cymene})]_2$ with K_2CO_3 .²⁰ *N*-Coordination (or *O*-coordination) of ruthenium species to **1a** should lead to **A1** (or **A2**)²¹ that after ring opening could form **B**. Hydroxylation followed by release of protons or dihydrogen would lead to **C**, which after decarboxylation would form ruthenacycle **D**.²² Protonolysis might lead to **E** that is in equilibria with **2a**; and the ruthenium catalyst is regenerated.

Different *N*-substituted phthalimide derivatives (**1**) conveniently provided the corresponding amides (**2-3**, Scheme 1). Aliphatic chains in the *N*-side are well tolerated although their bulkiness has a direct impact in the conversion. ^{*n*}-Butyl-substituted phthalimide **2b** was obtained in 50% yield, and the bulkier ^{*i*}-propyl-substituted phthalimide **2c** in 24% yield. These yields were improved by increasing the reaction time to 24 h (88% yield of **2b**) and the catalyst loading to 2.5 mol % too (87% yield of **2c**). The sterically-congested adamantyl-substituted phthalimide **2d** was not formed. Aliphatic chains appended with a cyano group provided **2e** in a good yield (63%), which was increased to 91% after 24 h of reaction time. Aliphatic chains containing other C–O bonds such as ethers, ketones and esters were compatible under the catalytic conditions, enabling the formation of the corresponding amides **2f**, **2g** and **2h** in 98%, 73% and 26% isolated yields, respectively. In the former case (**2h**), a higher yield of 50% was obtained when performing the catalysis during 24 h and 2.5 mol % catalyst loading. Notably, the ruthenium catalyst is site-selective by performing the protodecarbonylation in the phthalimide skeleton without interfering with other C–O and C=O bonds. When the *N*-substituent of the phthalimide contains aromatic moieties with different functional groups at the *para*-position (methyl, methoxy, fluoro, ketone, ester and nitro), isolated yields of 80%–98% of the corresponding amides **2i**–**2o** were obtained. Bromide- and iodide-containing phthalimides were converted into amides **2p** and **2q**, although the dehalogenated product (**2i**) was observed in 26% and 76% yields, respectively. *meta*-Substituted phenyl groups with a methoxy moiety were also compatible, leading to **2r** in 97% yield. *N*-Substituted phenyl groups containing *ortho* substituents gave good conversions. The chloro-derivative **2s** was isolated in 63% yield (no dechlorination was observed) and the methyl derivative **2t** in 89% yield. A methoxy group incorporated at the *ortho* position of the *N*-substituted phenyl moiety yielded **2u** in a poor 34%, likely due to inhibition by chelation to the catalyst. Nevertheless, the yield was increased to 78% by performing the catalysis during 48 h using 5 mol % of $[\text{RuCl}_2(p\text{-cymene})]_2$. A naphthalene group was also compatible (**2v**, 92% yield). The very coordinating quinoline-containing amide **2w** was obtained in 33% yield after 48 h reaction time using 5 mol % of $[\text{RuCl}_2(p\text{-cymene})]_2$, indicating

that relevant heterocyclic motifs are compatible under the studied reaction conditions. Benzyl fragments bearing different functional groups (methyl, cyano and trifluoromethyl) were also tolerated, leading to **2x**–**3a** in 90%–99% yields. The structure of **2x** was further confirmed by X-ray crystallographic analysis (see SI). The benzylpyridine-containing amide derivative **3b** was isolated in 88% yield, and the thiophene-containing amide **3c** in 60% yield after 48 h reaction time and 5 mol % of catalyst. The efficiency of the catalytic reaction enabled a double protodecarbonylation (**3d**) in 93% yield. Hydroxyl-containing phthalimides led to unknown mixtures of products, and a substrate containing a C=C double bond afforded the hydrogenated starting material in low yield due to the formation of H_2 during the catalysis. The steric effects and the coordinating properties of the substituents may account for those very few cases where the yields were low. Interestingly, by simply increasing the reaction time and the catalyst loading, high yields were obtained even for these reluctant substrates.

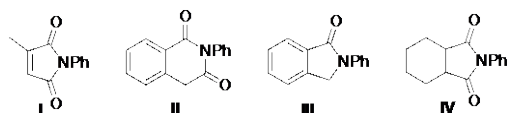
Scheme 1. Substrate Scope^{a,b}



^aAs Table 1, entry 1. ^bIsolated yields. ^c24 h reaction time. ^d2.5 mol % of $[\text{RuCl}_2(p\text{-cymene})]_2$. ^eProduct not isolated, yield estimated by ¹H NMR spectroscopy analysis. ^f48 h reaction time. ^g5 mol % of $[\text{RuCl}_2(p\text{-cymene})]_2$. ^hRatio of isomers determined by NMR spectroscopy analysis.

The selectivity of the catalysis with *N*-phenyl phthalimides containing substituents at 3' and 4' position was studied since two possible isomers could form (Scheme 1). Phthalimides containing fluoro, chloro and nitro groups at the 3' position led exclusively to the *meta* isomers **3e**–**3g**, respectively, with no evidence by TLC, ¹H NMR spectroscopy and GC-MS analysis

for the formation of other isomers. The halide-containing amides **3e** and **3f** were obtained in *ca.* 65% yield and the nitro-containing amide **3g** in 87% yield. By increasing the reaction time to 24 hours, **3e** was obtained in 93% yield. A phthalimide substituted at the 3' position with a methyl group (**3h**) provided a mixture of *ortho* and *meta* isomers in 38:62 ratio with an overall yield of 92%. This indicates that electron-withdrawing groups such as nitro at 3' position enhance the cleavage of the carbonyl group at the *ortho* position (with respect to 3' position). On the other hand, substituents at the 4' position (**3i-k**) have little impact on the selectivity, and mixture of isomers of similar ratios (*ca.* 60:40) were observed. The conversions of the phthalimides were found to depend on the electronic properties of the substituents at the 4' position. By decreasing the electron-donating capabilities of the substituents (Me > F > NO₂), the yield of the corresponding amides (**3k**, **3i** and **3j**) decreased from 98% to 82% to 49%, respectively. Phthalimide and phthalic anhydride benzamide and benzoic acid in 17% and 51%, respectively; and substrates **I-IV** that are structurally related to **1** did not follow protodecarbonylation.



In summary, a general, chemoselective ruthenium-catalyzed reaction enabling the conversion of phthalimides into amides has been developed. The mechanism, which does not follow a standard hydrogenation pathway,^{16a} involves a key decarboxylation step, with water serving as the source of protons. Since the reaction is operationally simple and proceeds without any pressure of H₂, it can be carried out in conventional laboratories with minimal risks. This work represents a new entry for the activation and further functionalization of challenging C–C(O) and C–N(R₂) bonds. Because the synthesis of amides and phthalimides is appealing in many scenarios relevant to chemistry and biology,²³ we anticipate that the presented method will inspire new synthetic shortcuts.

ASSOCIATED CONTENT

Supporting Information.

The Supporting Information is available free of charge on the ACS Publications website at DOI: XXX.

Experimental data and characterizations of compounds (PDF)
Crystallographic data for **2x** (CIF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

This work was financially supported by CNRS, Université de Rennes 1, China Scholarship Council (PhD grant to Y.-C.Y.) and Fondation Rennes 1 (Master grant to R. K.).

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