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A General and Convenient Method for the Rhodium-Catalyzed Decarbonylation of Aldehydes

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Abstract: A practical protocol for the decarbonylation of a wide range of aldehydes has been developed by using commercially available $RhCl_3 \cdot 3H_2O$ and dppp in a diglyme solution. This method gives rise to decarbonylated products in good to high yield and is particularly useful because of its experimental simplicity, high generality and excellent level of functional group tolerance. The reaction has been applied in a tandem Oppenauer oxidation-decarbonylation sequence, which removes a hydroxymethyl group in one operation.

Keywords: aldehydes; decarbonylation; Oppenauer oxidation; rhodium; tandem reaction

Introduction

In 1965 Tsuji and Ohno described the decarbonylation of aldehydes with stoichiometric amounts of Wilkinson's catalyst $[Rh(PPh_3)_3Cl]$.[1] Three years later the same authors reported the first example of a rhodium-catalyzed decarbonylation with 0.5% of $Rh(CO)(PPh_3)_2Cl$ at temperatures above 200 °C.[2] The high temperature did cause some side reactions and in 1978 Doughty and Pignolet described a milder procedure with $Rh(dppp)_2Cl$ [dppp = 1,3-bis(diphenylphosphino)propane].[3] This catalyst was shown to perform the decarbonylation of heptanal and benzaldehyde at temperatures between 115 and 178 °C.[3] However, $Rh(dppp)_2Cl$ is not commercially available, which may explain why relatively little work has been published on the application of this method. There are only a few examples in the literature where aldehydes have been decarbonylated with $Rh(dppp)_2Cl$ and in some of these cases the catalyst was generated *in situ* from dppp and another Rh(I) complex $\{Rh(CO)(PPh_3)_2Cl$ or $[Rh(COD)Cl]_2\}$.[4] Moreover, there are also examples where the catalytic decarbonylation with $Rh(dppp)_2Cl$ has failed apparently due to decomposition of the catalyst due to its high sensitivity towards air.[5] More recently, $Rh(CO)(triphos)SbF_6$ was shown to decarbonylate aldehydes,[6] but this catalyst is not easy to prepare. As a result, stoichiometric amounts of Wilkinson's catalyst are still being used for decarbonylation of aldehydes in many total synthesis projects.[7] Based on these observations we decided to search for a more practical catalytic method. Herein, we describe the development of a more convenient procedure for the decarbonylation of aldehydes by the use of commercially available reagents.

Results and Discussion

The initial studies were carried out with $Rh(dppp)_2Cl$ and 2-naphthaldehyde. $Rh(dppp)_2Cl$ is prepared by ligand exchange from $Rh(COE)_2Cl$, which is available in one step from $RhCl_3 \cdot 3H_2O$.[8] Unfortunately, $Rh(dppp)_2Cl$ is poorly soluble in organic solvents like dioxane, toluene and xylene. Addition of water improved the solubility and it was found that a 10:1 mixture of dioxane and water dissolved the catalyst completely. However, decarbonylation of naphthaldehyde at reflux in this mixture was very sluggish and required several days for complete conversion. Furthermore, the reaction was difficult to reproduce under these conditions. The decarbonylation was then performed in a closed vessel at 200 °C in a microwave oven. To our delight this experiment gave full conversion of naphthaldehyde in 30 min with 5% of $Rh(dppp)_2Cl$. The same result was obtained with 5% of $Rh(COE)_2Cl$ in the presence of 10% of dppp while $Rh(COE)_2Cl$ or $Rh(PPh_3)_3Cl$ in the absence of other phosphine ligands only gave 10% conversion after 30 min. Interestingly, the active catalyst could also be

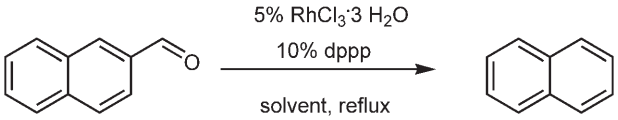
generated *in situ* from commercially available $RhCl_3 \cdot 3H_2O$. Treatment of naphthaldehyde with 5% of $RhCl_3 \cdot 3H_2O$ and 10% of dppp in the microwave oven at 200 °C gave complete conversion into naphthalene in 30 min. During the experiment the pressure in the vial increased to about 20 bars since carbon monoxide is produced in the course of the reaction. This makes it difficult to use a closed system for the decarbonylation and may also lead to deactivation of the rhodium catalyst. Therefore, different high boiling solvents were screened to find a suitable alternative to the dioxane/water mixture (Table 1).

The fastest reactions were observed by using diglyme or NMP with full conversion after 3 h (entries 1 and 2) whereas DMSO inhibited the reaction (entry 3). In mesitylene, heptanol, diisobutyl ketone and ethyl hexanoate (entries 4–7) the reaction also went to completion, but reaction times of 10–20 h were required. Accordingly, we selected diglyme as the solvent of choice, since it allows a lower and more constant reaction temperature than NMP.

With this procedure in hand a number of experiments were then conducted in order to identify the optimal phosphine ligand (Figure 1). We applied mono-, bi- and tridentate phosphine ligands as well as one aminophosphine ligand in the decarbonylation with $RhCl_3 \cdot 3H_2O$.

The initial results with monodentate ligands [PPh_3, PCy_3, P(*o*-furyl)$_3$ and PCy_2(2-biphenyl)] all gave conversions below 20%. Similarly, the tridentate ligands **1** and **2** gave almost no conversion when the active catalyst was generated *in situ*. Thus, only bidentate ligands were further studied (Table 2).

Table 1. Rhodium-catalyzed decarbonylation of 2-naphthaldehyde using different solvents.[a]



Entry	Solvent	Boiling point	Time to reach full conversion[b]
1	Diglyme	162 °C	3 h
2[c]	NMP	202 °C	3 h
3	DMSO	189 °C	-[d]
4	Mesitylene	164 °C	20 h
5	Heptanol	176 °C	10 h
6	Diisobutyl ketone	168 °C	10 h
7	Ethyl hexanoate	166 °C	10 h

[a] *Reaction conditions:* Naphthaldehyde (1.0 equiv.), $RhCl_3 \cdot 3H_2O$ (5 mol%), dppp (10 mol%) in the corresponding solvent at reflux under argon.
[b] By GC-MS.
[c] Heated to 190 °C.
[d] Stalled after 24 h at 3% conversion.

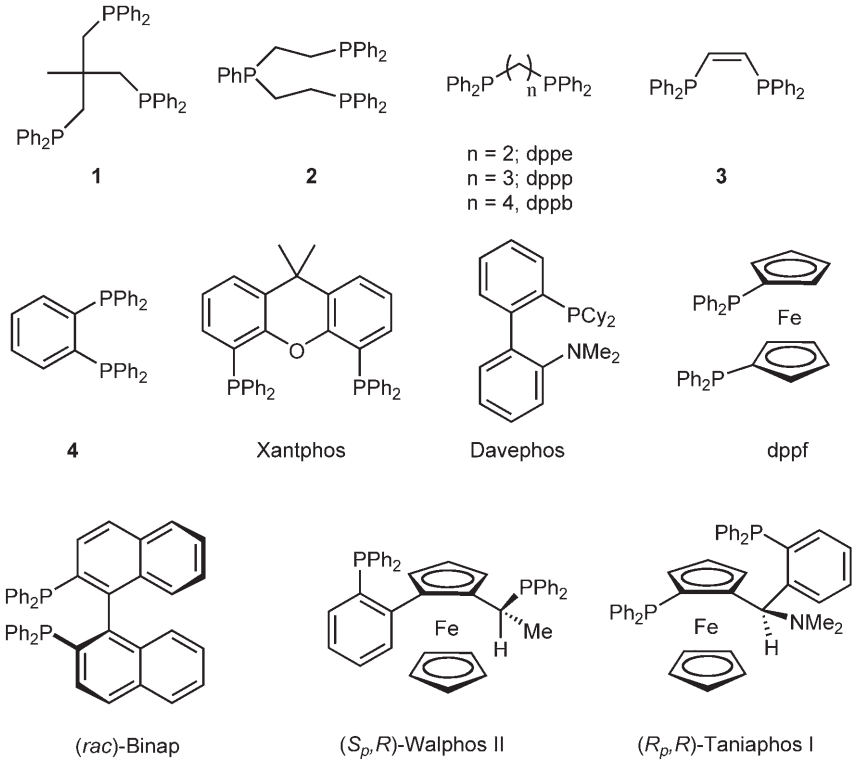


Figure 1. Phosphine ligands tested.

Table 2. Rhodium-catalyzed decarbonylation of 2-naphthaldehyde using different ligands.[a]

Entry	Ligand	Time	Conversion[b]	Bite angle (standard deviation)[c]
1	**1**	3 h	<5%	
2	**2**	3 h	<5%	
3	dppe	3 h	<5%	85° (3°)
4	dppp	3 h	quant.	91° (2°)
5	dppb	6 h	quant.	98° (5°)
6	**3**	3 h	<5%	
7	**4**	3 h	<5%	83° (3°)
8	Xantphos	6 h	61%	104–107°
9	Davephos	6 h	20%	
10	dppf	3 h	quant.	96° (2°)
11	BINAP	3 h	quant.	92° (3°)
12	Walphos II	6 h	75%	
13	Taniaphos I	3 h	quant.	

[a] *Reaction conditions:* Naphthaldehyde (1.0 equiv.), $RhCl_3 \cdot 3H_2O$ (5 mol%), ligand (10 mol%) in diglyme at reflux under argon.
[b] By GC-MS.
[c] Bite angle according to the literature.[9]

When using the homologous ligands dppe, dppp, and dppb, a maximum in reactivity was observed for dppp. Only traces of product were observed with **3** and **4**, which have a more rigid backbone and a smaller bite angle. The more flexible ligand Xantphos[9] with a large bite angle of 104–107° gave an improved reactivity (61% yield after 6 h) but was still not comparable to dppp whereas the mixed P,N ligand Davephos[10] resulted in only minor amounts of the desired product. When dppf or BINAP were used, the decarbonylation went to completion in 3 h. Surprisingly, the decarbonylation of naphthaldehyde with Solphos,[11] a structural analogue of BINAP resulted in only traces of naphthalene. The chiral ferrocene ligands Walphos II[11] and Taniaphos I[11] showed a high reactivity with the latter having a similar reactivity as dppp. The best ligands for the reaction, dppp, dppf, BINAP and Taniaphos I, all have an average bite angle between 91 and 96°[9] and have a rather flexible backbone. Bidentate ligands with smaller bite angles like dppe, **3**, and **4** gave almost no conversion while Xantphos and dppb with a larger bite angle reacted slowly. Hence, the most reactive ligands were dppp, dppf, BINAP and Taniaphos I. However, in the reaction with dppf the mixture quickly turned black which indicates that either the ligand or the active rhodium catalyst is not sufficiently stable. With dppp, BINAP and Taniaphos I the reaction mixture maintained a clear yellow color with no sign of metal precipitation.

To better quantify the catalytic activity of the different ligands, we performed kinetic measurements to determine the turnover frequency and compared the results to the preformed catalyst using phenylacetaldehyde as the starting material. Applying standard conditions with 0.05 mol% of rhodium catalyst gave no conversion with the preformed catalyst, whereas full conversion was achieved with the *in situ* formed dppp catalyst. Even degassing of the reaction mixture for 1 h by sonication under an argon atmosphere was not sufficient to get any conversion with 0.05 mol% of $Rh(dppp)_2Cl$. Only a thorough degassing of the solvent by refluxing overnight under an argon atmosphere and subsequent addition of the catalyst and the starting material lead to full conversion of the starting material with 0.05 mol% of $Rh(dppp)_2Cl$. For the purposes of comparison, this procedure was also applied for the *in situ* formed catalysts with dppp, dppf and BINAP. The preformed catalyst $Rh(dppp)_2Cl$ and the *in situ* formed catalysts with dppp and BINAP showed full conversion towards the desired product within 24 h. Fastest reacting was the preformed system with a turnover frequency (TOF) of $575\ h^{-1}$ compared to the *in situ* formed systems with TOFs of $450\ h^{-1}$ for BINAP and $390\ h^{-1}$ for dppp. On the other hand, the preformed catalyst with dppf initially showed the fastest reaction of all the *in situ* formed catalyst with a TOF of $560\ h^{-1}$ but after 1 h the reaction mixture started to turn dark and the formation of toluene ceased while at the same time the formation of (*Z*)-2,4-diphenylbut-2-enal, an aldol condensation product, started. Work-up after 24 h showed full consumption of the starting material and a mixture of toluene and (*Z*)-2,4-diphenylbut-2-enal. Hence for the preformed system as well as for the *in situ* formed systems with dppp and BINAP a TON of >2000 could be achieved. While the preformed catalyst showed an approximately 1.5 times faster reaction than the *in situ* formed catalyst, the *in situ* formed catalytic system showed a much higher tolerance towards air than the preformed catalyst. Since dppp reacts more or less as fast as BINAP and is much cheaper we selected this ligand for general use.

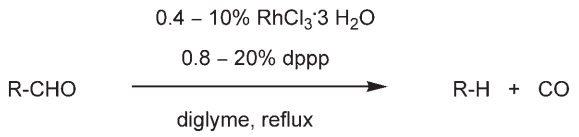
To examine the reducing agent with the *in situ* formed catalyst we carried out ^{31}P NMR experiments in deuterated diglyme. Thus, $RhCl_3 \cdot 3H_2O$ and 2 equivalents of dppp were heated to reflux in deuterated diglyme under argon in the presence and in the absence of 1 equivalent of benzaldehyde. NMR samples were taken out and measured at 60 °C. Due to the much lower sensitivity of the rhodium-coordinated phosphines and a partial precipitation of the rhodium-complex by cooling from 162 °C to 60 °C we were only able to observe the non-coordinated phosphines. A spectrum of $Rh(dppp)_2Cl$ could only be obtained by using D_2O as a co-solvent. Reaction of $RhCl_3 \cdot 3H_2O$ with dppp and aldehyde showed after 1 min four singlet signals at −16.2 ppm (identified as dppp), 29.5 ppm (identified as dppp dioxide) and

−16.4 ppm and 28.6 ppm (most likely the dppp monoxide, which showed −17.5 ppm and 28.7 ppm in pure diglyme). After 10 min the signal of the free dppp and the dppp monoxide disappeared leaving only dppp dioxide in solution which shows that $RhCl_3$ is reduced by dppp which in turn is oxidized to non-coordinating dppp dioxide. The spectra in the absence of benzaldehyde showed the same result confirming that the aldehyde is not involved in the reduction.

To determine the scope and limitations of the decarbonylation procedure several different aldehydes were subjected to the optimized conditions (Table 3).

Aldehydes containing ether, ester, amino, cyano, amide and imide groups as well as chlorides and fluorides are converted to the corresponding decarbonylated products. Both electron-poor (entries 2–5) and electron-rich (entries 7–9) aromatic compounds reacted in good to high yield. The slightly lower yields of α,α,α-trifluorotoluene (entry 3, 78%), chlorobenzene (entry 4, 83%), toluene (entry 7, 76%), anisole (entry 8, 74%), and ethylbenzene (entry 13, 70%) were caused by work-up problems due to the volatility of the products. In some cases, the products were isolated by direct distillation from the reaction mixture, but some product always remained in the diglyme solution as shown by GC analysis. *p*-Nitrobenzaldehyde partially decomposed during the reaction and the work-up (entry 6) and only gave 12% isolated yield together with some reduced by-products. Extension of the procedure towards enolizable aliphatic aldehydes proceeded smoothly and gave nonane (entry 10) and *p*-xylene (entry 11) in high yields (90% and 81%, respectively) with no sign of a competing aldol reaction. The decarbonylation of an α,β-unsaturated aldehyde (entry 12) could also be achieved in

Table 3. Decarbonylation of aldehydes.



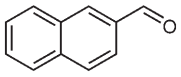
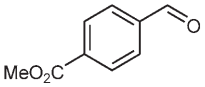
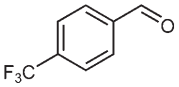
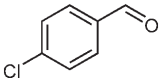
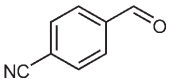
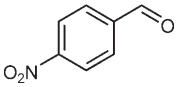
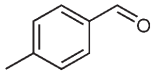
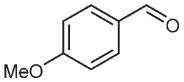
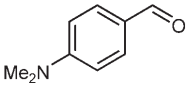
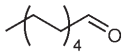
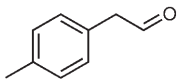
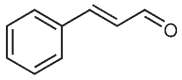
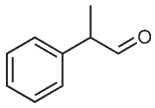
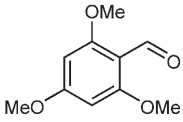
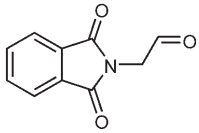
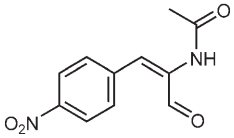
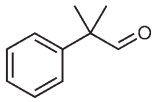
Entry	Aldehyde	Method[a]	Yield[b]
1		A	84%
2		A	87%
3		B	78%[c]
4		B	83%[c]
5		A	93%
6		A	12%
7		B	76%[c]
8		A	74%[c]
9		A	97%
10		A	90%
11		A	81%[c]

Table 3. (Continued)

Entry	Aldehyde	Method[a]	Yield[b]
12		A	87%
13		A	70%[c]
14		A	94%
15		C	87%
16		C	67%
17		A	traces

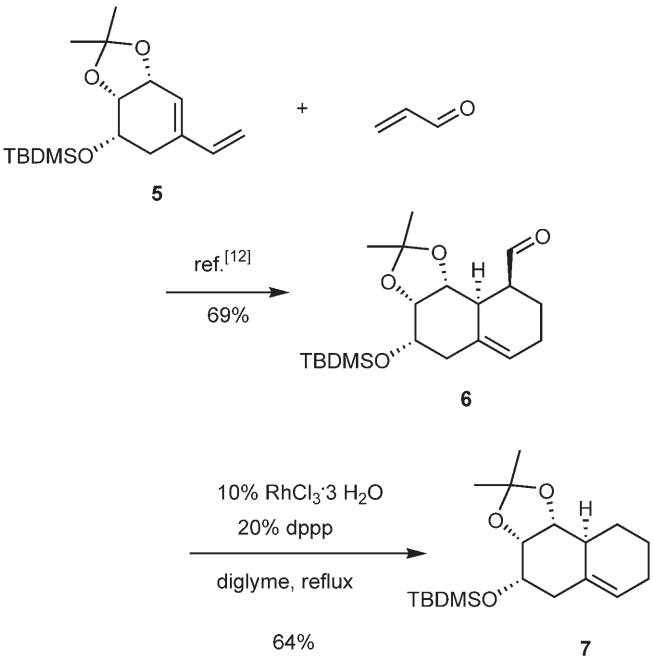
[a] Method A: A solution of the aldehyde (10.0 mmol), $RhCl_3·3H_2O$ (0.04–1.0 mmol) and dppp (0.08–2.0 mmol) in diglyme was heated to reflux under argon. The product was isolated by diluting the mixture with pentane and washing 5 times with water to remove diglyme. Purified by flash chromatography. Method B: As in A, but the product was isolated by continuous distillation from the reaction mixture. Method C: As in A, but diglyme was removed by kugelrohr distillation followed by purification with flash chromatography.

[b] Isolated yield.

[c] Decreased yield due to the volatility of the product.

high yield (87%). More sterically demanding aldehydes like the α-branched hydratropaldehyde (entry 13) and the di-*ortho*-substituted 2,4,6-trimethoxybenzaldehyde (entry 14) were decarbonylated in good to excellent yields (70% and 94%). (Phthalimidyl)acetaldehyde (entry 15) was also a good substrate and was decarbonylated in a high yield (87%) without attack on the imide group. Even the decarbonylation of the more complicated aldehyde in entry 16 with a double bond as well as a nitro and an amido group succeeded in a good yield (67%) despite the problematic nitro group. On the other hand, the α,α-dibranched aldehyde in entry 17 was a poor substrate for the reaction yielding only traces of the desired product.

To further expand the synthetic utility of the reaction we decided to investigate the decarbonylation of aldehyde **6** (Scheme 1).

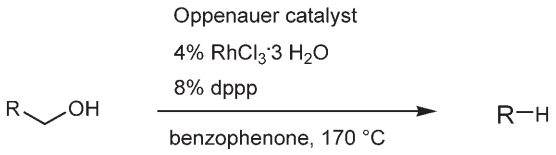


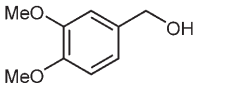
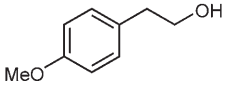
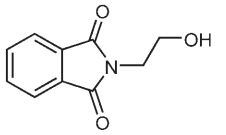
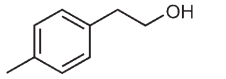
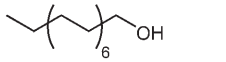
Scheme 1. Consecutive Diels–Alder-decarbonylation reaction.

This compound was recently prepared in our laboratory by a Diels–Alder reaction between diene **5** and acrolein.[12] Treatment of **6** with $RhCl_3 \cdot 3H_2O$ and dppp gave clean decarbonylation into decalin derivative **7** without loss of the protecting groups or rearrangement of the double bond. The overall result of this two-step sequence is the addition of ethylene to diene **5**, a transformation which is not feasible by a one-step cycloaddition reaction due to the large HOMO-LUMO gap.

We also performed the decarbonylation in combination with the Oppenauer oxidation.[13] Hereby, a primary alcohol is converted into the corresponding aldehyde, which is then decarbonylated in the same reaction mixture (Table 4).

Table 4. Tandem Oppenauer-type oxidation-decarbonylation reaction.[a]



Entry	Alcohol	Solvent	Catalyst	Yield[c]
1[b]		Mesitylene	Al(O-*t*-Bu)$_3$	54%
2[b]		Mesitylene	Al(O-*t*-Bu)$_3$	56%
3[b]		Mesitylene	Al(O-*t*-Bu)$_3$	26%
4		Benzophenone	$[Cp^*IrCl_2]_2$/K_2CO_3	73%
5		Benzophenone	$[Cp^*IrCl_2]_2$/K_2CO_3	63%[d]

[a] *Reaction conditions:* Alcohol (1.0 equiv.), $RhCl_3 \cdot 3H_2O$ (4 mol%), dppp (8 mol%), K_2CO_3 (20 mol%), $[Cp^*IrCl_2]_2$ (2 mol%) in benzophenone at 170°C under argon.

[b] *Reaction conditions:* Alcohol (1.0 equiv.), $RhCl_3 \cdot 3H_2O$ (5 mol%), dppp (10 mol%), Al(O-*t*-Bu)$_3$ (30 mol%), benzophenone (3.0 equiv) in mesitylene at reflux under argon.

[c] Isolated yield.

[d] 25% of tetradecene was also formed.

Initially, 3,4-dimethoxybenzyl alcohol (Table 4, entry 1) was reacted under the classical Oppenauer conditions with aluminum tris(*tert*-butoxide) and benzophenone in a mesitylene solution containing $RhCl_3 \cdot 3H_2O$ and dppp, and the mixture was heated until the decarbonylation had gone to completion. However, this only resulted in 54% yield of the decarbonylated product and the major problem seemed to be the oxidation to the aldehyde. Similar unsatisfactory results were obtained with 2-(4-methoxyphenyl)ethanol and 2-(phthalimidyl)ethanol, which gave only poor to moderate yields (entries 2 and 3). Changing the solvent to NMP or diglyme resulted in negligible product formation. Therefore, we decided to change the conditions for the hydrogen transfer oxidation which can also be achieved with various transition metal catalysts, for example, the iridium complex $[Cp^*IrCl_2]_2$ in the presence of potassium carbonate.[14] In fact, treatment of 2-(4-methylphenyl)ethanol with $[Cp^*IrCl_2]_2$, $RhCl_3 \cdot 3H_2O$ and dppp in benzophenone gave 73% of *p*-xylene and the tandem reaction

went to completion without the addition of additional catalyst during the course of the reaction (entry 4). The tandem process also worked for a long-chain aliphatic alcohol although an olefin was formed as a by-product in this case (entry 5).

Conclusions

In summary, we have established a versatile and easy to handle procedure for the rhodium-catalyzed decarbonylation of aldehydes by using commercially available $RhCl_3 \cdot 3H_2O$ and dppp. The reaction tolerates a wide range of functional groups and can be applied to both aromatic and aliphatic aldehydes. This procedure was also successfully used in a Diels–Alder decarbonylation sequence, which introduces acrolein as an ethylene synthon for the Diels–Alder reaction. Furthermore, we were able to employ the methodology in a tandem Oppenauer-type oxidation-decarbonylation reaction, which makes it possible to remove a hydroxymethyl group in one step. Currently, the mechanism of the decarbonylation reaction is being studied in further detail.

Experimental Section

General Remarks

All chemicals were purchased from commercial sources and used without purification. All reactions were carried out under an inert atmosphere. Flash column chromatography was performed with silica gel 60 (particle size 0.040–0.063 mm). ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian Mercury 300 spectrometer. Chemical shifts are reported in parts per million (ppm) with the solvent chloroform as the internal standard (^{1}H NMR $CHCl_3$ $\delta_H = 7.26$ ppm and ^{13}C NMR $CDCl_3$ $\delta_C = 77.0$ ppm). IR spectra were recorded on a Perkin–Elmer 1600 Series FT-IR using KBr plates. EI-MS were recorded on a Shimadzu GCMS-QP5000 with a direct inlet. ESI-HR-MS were recorded on a Ionspec 4.7 Telsla Ultima FT-MS.

General Procedure for the Decarbonylation of Aldehydes

To a 50-mL flask were added the aldehyde (10.0 mmol), $RhCl_3 \cdot 3H_2O$ (0.3 mmol, 3 mol%), dppp (0.6 mmol, 6 mol%), and diglyme (25 mL). The flask was equipped with a Liebig condenser and then evacuated and subsequently flushed with argon. This procedure was repeated three times. The flask was put into a pre-heated oil bath and the reaction mixture was heated to reflux (162 °C) and kept at reflux for 16 h. After cooling, the mixture was diluted with pentane (30 mL) and washed with water (5 × 20 mL) and then dried (Na_2SO_4). The solvent was carefully evaporated under reduced pressure and the decarbonylated products were purified by column chromatography on silica gel.

General Procedure for the Oppenauer-Type Oxidation Decarbonylation Reaction

To a 25-mL flask were added the primary alcohol (2.0 mmol), $RhCl_3 \cdot 3H_2O$ (0.08 mmol, 4 mol%), dppp (0.16 mmol, 8 mol%), $[Cp^*IrCl_2]_2$ (0.04 mmol, 2 mol%), K_2CO_3 (0.4 mmol, 20 mol%) and benzophenone (10 g). The flask was equipped with a Liebig condenser and then evacuated and subsequently flushed with argon. This procedure was repeated three times. The flask was put into a pre-heated oil bath and the reaction mixture was heated to 170 °C for 1–4 days. After cooling to approximately 50–60 °C the solution was put on a silica gel column and purified by flash chromatography.

N-(*E*)-(4-Nitrostyryl)acetamide (Table 3, entry 16)

Synthesized according to the general procedure on a 0.16-mmol scale affording a yellow solid; yield: 24 mg (0.11 mmol, 67%); $R_f = 0.1$ (dichloromethane); ^{1}H NMR [300 MHz, $(CD_3)_2CO$]: $\delta = 9.68$ (d, $J = 10.5$ Hz, 1H, N*H*), 8.14 (d, $J = 8.6$ Hz, 2H, H-5), 7.76 (dd, $J = 14.7$, 10.5 Hz, 1H, H-1), 7.60 (d, $J = 8.6$ Hz, 2H, H-4), 6.27 (d, $J = 14.7$ Hz, 1H, H-2), 2.05 (s, 3H, CH_3); ^{13}C NMR [75 MHz, $(CD_3)_2CO$]: $\delta =$ 169.4 (*C*O), 146.5 (C-6), 129.8 (C-3), 127.4, 125.8 (C-4, C-5), 111.6, 110.6 (C-1, C-2), 23.9 (*C*H$_3$); MALDI-HR-MS: $m/z =$ 229.0589, calcd. for $C_{10}H_{10}N_2O_3Na$: 229.0589.

(1*R*,2*R*,3*S*,10*S*)-1,2-(Isopropylidenedioxy)-3-[(*tert*-butyldimethylsilyl)oxy]bicyclo[4.4.0]dec-5-ene (7)

Synthesized according to the general procedure on a 33 μmol scale affording a light yellow solid; yield: 7 mg (21 μmol, 64%); $R_f = 0.47$ (pentane/ethyl acetate, 4:1); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 5.60$–5.54 (m, 1H, H-6), 4.16 (dd, $J =$ 5.1, 3.9 Hz, 1H, H-2), 3.83 (ddd, $J = 10.5$, 4.7, 3.9 Hz, 1H, H-3), 3.73 (dd, $J = 9.0$, 5.1 Hz, 1H, H-1), 2.50–2.40 (m, 1H, H-10), 2.30–2.20 (m, 1H, H-4 or H-7), 2.14 (dd, $J = 12.9$, 4.7 Hz, 1H, H-4), 2.00–1.90 (m, 2H, H-4 or H-7), 1.90–1.80 (m, 1H, H-8 or H-9), 1.60–1.40 (m, 3H, H-8 or H-9), 1.54 (s, 3H, CH_3C), 1.36 (s, 3H, CH_3C), 0.91 (s, 9H, (CH_3)$_3$C), 0.10 (s, 3H, CH_3Si), 0.10 (s, 3H, CH_3Si); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 133.2$ (C-5), 124.7 (C-6), 109.1 [Me_2C(OR)OR], 74.8, 73.7, 71.2 (C-1, C-2, C-3), 38.1, 37.6 (C-4, C-10), 30.8 (C-7), 25.7 [(CH$_3$)$_3$*C*], 25.5, 20.4 (C-8, C-9), 18.0 [(*C*H$_3$)$_3$C], −4.7 (*C*H$_3$Si), −5.0 (*C*H$_3$Si).

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