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ARTICLE

Triphenylphosphine mediated photo-rearrangement and methanol addition of aryl chalcones to 1-propanones

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Qiu Sun,[a] Chang Jiang Yao[a,b] and Burkhard König[a*]

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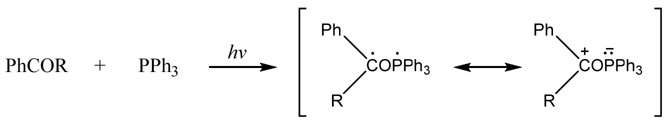
Aryl chalcones rearrange and add methanol giving substituted propane-1-ones upon UV-A irradiation in the presence of PPh_3. We propose two possible mechanisms for this photo-rearrangement. The reaction involves either the formation of a phosphine-carbonyl intermediate, nucleophilic addition of MeOH and 1, 2 aryl migration or the formation of ylide and carbene intermediates. Intermediates trapped from the reaction mixture support the first mechanistic hypothesis.

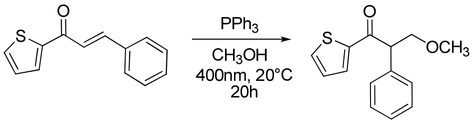
Introduction

The photo chemistry of chalcones has always attracted the interest of organic chemists and in recent years particular the reactions of aryl enones under visible light photoredox catalysis were studied.[1-10] Typical reaction conditions use a ruthenium complex as visible light absorbing photoredox catalyst and a tertiary amine as sacrificial electron donor to initiate a photoinduced electron transfer reducing the enone to the corresponding radical anion, which undergoes e.g. inter- or intramolecular [2 + 2] cycloaddition[4, 7] or a reductive coupling.[9] The photochemistry of aryl ketones in the presence of PPh_3 was studied already more than 40 years ago,[11-14] but investigations focused on the photogeneration of ylides[15] and Norrish type II reactions.[14] Pandey et al. described in 1997 a photocatalytic system for the reductive cyclizations of enones, where 9,10-dicyanoanthracene (DCA) were employed as photoredox catalyst and PPh_3 as sacrificial electron donor.[16] In addition to its role as electron donor similar to tertiary amines, PPh_3 has some unique properties: It is sterically more hindered; it is no hydrogen atom donor and an efficient quencher of the carbonyl triplet state (**Scheme 1**). Therefore the photochemical behavior of α, β-unsaturated ketones in the presence of PPh_3 caused our interest.



Scheme 1. Photolysis of aryl ketones in the presence of PPh_3.

We investigated the photoreaction of a variety of chalcone derivatives in the presence of PPh_3 applying different solvents, catalysts and light sources. The reaction of chalcone **1a** with 10 mol % of DCA and PPh_3 (1 equiv.) in MeOH after 20h irradiation at 400 nm gave an unexpected rearrangement and methanol addition product **2a** (**Scheme 2**) instead of the expected cyclization or Michael addition product. Further studies showed that the reaction proceeds without addition of a photosensitizer, but not in the dark indicating a direct photochemical process. Similar rearrangements have been performed using hypervalent iodine[17, 18] or thallium reagents through oxidative processes.[19] However, since PPh_3 is not an oxidative reagent, we propose a different mechanism and developed a convenient experimental procedure for the interesting rearrangement.

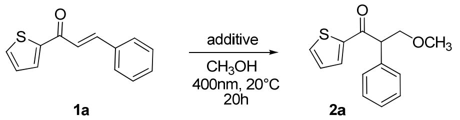


Scheme 2. Photo-rearrangement and methanol addition of 2-thienyl chalcone **1a**.

Results and discussion

Initially the required amount of PPh_3 for the photoreaction was investigated (**Table 1**). The desired product was obtained in 84% yield with 0.5 equiv. of PPh_3. Decreasing the amount of PPh_3 to 0.25 equiv. does not reduce the product yield, but with catalytic amounts of less than 10 mol% PPh_3, the yield of the reaction dropped to 28%. During work up 30 to 40% of the PPh_3 could be recycled by column chromatography. Triphenylphosphine oxide was isolated as a byproduct. The results indicate that PPh_3 acts as a catalyst, but decomposes during the reaction yielding PPh_3=O. Using PPh_3=O, $PHPh_2$ and DIPEA (*N*,*N*-diisopropylethylamine) instead of PPh_3 did not yield the desired product **2a**, but the formation of small amounts of [2 + 2] cycloaddition product was observed (see supporting information). Control experiments without PPh_3, without light or under reflux conditions gave no product revealing that PPh_3 and light are essential (entries 8, 9 and 10). The solvent MeOH was replaced by EtOH, i-PrOH or CF_3CH_2OH, but no product formation was detected in these solvents by GC-MS analysis of the reaction mixture. Besides, the reaction was also carried out with photosensitizers, e.g., $Ru(bpy)_3Cl_2·6H_2O$ and Eosin Y, at 450 nm and 530 nm respectively. The formation of [2 + 2] cycloaddition product and a reductive coupling product was observed when $Ru(bpy)_3Cl_2·6H_2O$ was used in the reaction, while no reaction occurred, when it was irradiated with Eosin Y at 530 nm.

Table 1: Investigation of different reaction conditions for the photo-rearrangement/addition reaction of **1a.**

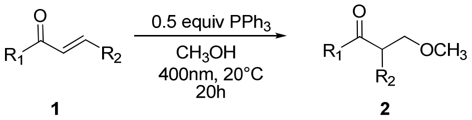


Entry	Conditions	Yield[%]$^{[a][b]}$
1	PPh_3 (1.0 equiv)	56
2	PPh_3 (0.5 equiv)	84
3	PPh_3 (0.25 equiv)	73
4	PPh_3 (0.10 equiv)	28
5	PPh_3=O (1.0 equiv)	0
6	$PHPh_2$ (1.0 equiv)	0
7	DIPEA (1.0 equiv)	0
8	no PPh_3	0
9	PPh_3 (1.0 equiv), no light	0
10	PPh_3 (1.0 equiv), no light, reflux	0

[a] Isolated yield. [b] The reactions were carried out in 1.0 mL of CH_3OH under N_2 atmosphere.

Next, we investigated the substrate scope of aryl chalcones for the photoreaction and the results are summarized in **Table 2**. Phenyl and naphthyl chalcones rearrange using the described reaction conditions. The X-ray structure analysis of compound **2n** confirmed its structure (**Figure 1**) as assigned from spectroscopic data. Chalcones bearing moderate electron withdrawing, neutral and electron donating substituents reacted smoothly affording the corresponding products in moderate to good yields. Strong electron withdrawing and donating substitutes like $-OCH_3$, $-NO_2$ and -CN on either aromatic ring inhibit the rearrangement reaction; products of the [2 + 2] cycloaddition were observed in these cases (see supporting information).

Table 2: Scope of aryl chalcones in the photo-rearrangement/addition reaction.



Entry	Aryl-chalcone	R_1	R_2	Product	Yield [%]$^{[a],[b]}$
1	**1a**	2-thienyl	Ph	**2a**	84
2	**1b**	2-thienyl	4-F-C_6H_4	**2b**	42
3	**1c**	2-thienyl	4-Br-C_6H_4	**2c**	55
4	**1d**	2-thienyl	4-Cl-C_6H_4	**2d**	37
5	**1e**	2-thienyl	3-Br-C_6H_4	**2e**	32
6	**1f**	2-thienyl	4-Me-C_6H_4	**2f**	79
7	**1g**	2-thienyl	4-MeO-C_6H_4	**2g**	trace
8	**1h**	2-thienyl	4-CN-C_6H_4	**2h**	-
9	**1i**	Ph	Ph	**2i**	78
10	**1j**	Ph	4-Me-C_6H_4	**2j**	60
11	**1k**	4-MeO-C_6H_4	4-Br-C_6H_4	**2k**	-
12	**1l**	4-MeO-C_6H_4	Ph	**2l**	trace
13	**1m**	2-NO_2-C_6H_4	Ph	**2m**	-
14	**1n**	2-naphthyl	Ph	**2n**	48

[a] Isolated yield. [b] The reactions were carried out in 1.0 mL of CH_3OH under N_2 atmosphere.

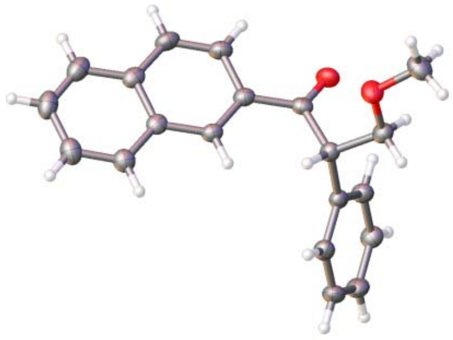
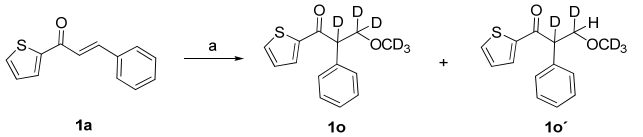


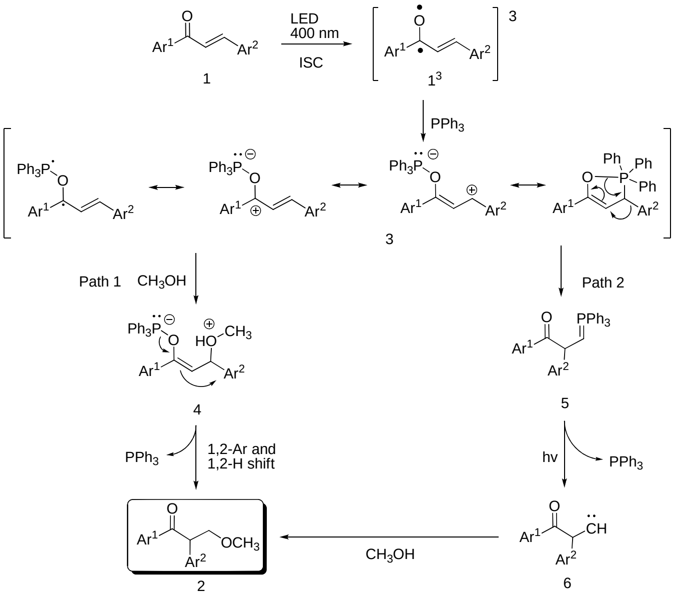
Figure 1. Structure of compound **2n** obtained from the photo-rearrangement/addition reaction of aryl chalcone **1n**, in the solid state.

Several reactions were performed to investigate the mechanism of the photo-rearrangement/addition reaction. Initially, the reaction was performed in deuterated methanol giving products 1o and 1o' in a ratio of approximately 5:1 (**Scheme 3**). The more acidic α-hydrogen atom is fully deuterated, while the less reactive β-hydrogen atoms are not completely exchanged by deuterium.



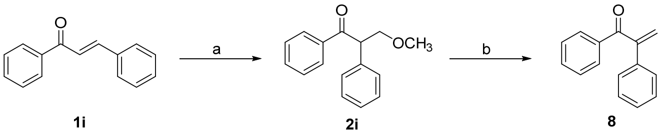
Scheme 3. Photo-rearrangement/addition reaction of **1a** in CD_3OD leads to deuterium incorporation. Reaction conditions: a) 0.5 equiv PPh_3, CD_3OD, 20°C, 20h.

The presence of the persistent radical 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) did not affect the reaction and no radical trapping products were identified indicating the absence of a radical mechanism. On the basis of related reports,[14, 15, 20] we propose two possible mechanisms shown in **Scheme 4**. The photochemical excitation of the α,β-unsaturated ketone **1** and ISC gives its triplet state $\mathbf{1}^3$, which is captured by PPh_3 forming **3** through the intervention of an exciplex. The electronic structure of compound **3** is described by four resonance structures. In pathway 1, compound **3** is nucleophilic attacked by the solvent MeOH giving intermediate **4**. 1,2-Aryl shift and 1,2-hydrogen shift provide the product **2** of a rearrangement addition reaction sequence. In pathway 2, 1,2-aryl migration occurres giving phosphonium ylide **5**. It is known that ylides can be photochemically cleaved to carbenes.[20] Carbene **6** is formed upon irradiation and quickly trapped by MeOH to give product **2**. Our attempts to identify the intermediate presence of a phosphonium ylide by reaction with benzaldehyde or of the carbene with styrene, cyclohexene and other alcohols were without success. We also did not observe any products arising from the carbene intermediate as described in previous reports.[14, 15] Intermediate **3** tends to react *via* O-P bond cleavage to the products.[21] The extended π system of the α,β-unsaturated ketone may stabilize the carbonyl group. Therefore, the mechanistic hypothesis of pathway 1 may be more likely, but we cannot rule out a reaction along pathway 2 from our experimental results.



Scheme 4. Suggested mechanistic hypothesis of the photo-rearrangement/addition reaction of aryl chalcones in the presence of PPh_3

To demonstrate a synthetic application, we used the photoreaction product **2i** for the synthesis of 2-substituted enone **3** (**Scheme 5**). Functionalized terminal enones are useful compounds in organic synthesis. They are highly reactive and can undergo conjugate addition reactions with nucleophiles yielding a variety of bioactive products. The reaction of chalcone **1i** with PPh_3 under standard photoreaction conditions provided the corresponding product **2i**, which was then further converted into 1,2-diphenylprop-2-en-1-one **8** by heating to 160-170°C with 1% $NaOCH_3$ in toluene.[22]



Scheme 5. Synthesis of the 2-substituted terminal enone **8** using the PPh_3 mediated photo-rearrangement/addition reaction of compound **1i** and subsequent elimination of methanol. Reaction conditions: a) 0.5 equiv PPh_3, CD_3OD, 20°C, 20h, 78%. b) 1% $NaOCH_3$, $PhCH_3$, 160-170°C, 1.5h, 72%.

Experimental

General

^1H, ^{13}C NMR spectra were obtained at 298 K using a Bruker AVANCE 300 spectrometer (operating at 300.13 MHz for ^1H and 75.47 MHz for ^{13}C), Bruker AVANCE 400 spectrometer (operating at 400.13 MHz for 1H and 100.62 MHz for 13C). The spectra were obtained using chloroform-d (99.8%, Deutero GmbH) and referenced against non-deuterated (^1H) / deuterated (^{13}C) solvents. The shift values (δ H and δ C) are always given in ppm with *J* values in Hz. The melting points were measured using a Stanford Research Systems OptiMelt MPA 100. The highresolution mass spectra were obtained using a Finnigan MAT SSQ 710 A spectrometer at 70 eV (HREIMS, positive and negative mode) or an Agilent 6540 UHD (HRESIMS, positive and negative mode). Automated flash chromatography was performed on a Biotage® IsoleraTM Spektra One device. Silica gel 60 M (40-63 µm, Merck) was used for the flash column chromatography. The starting materials and reagents were purchased from commercial suppliers and used without further purification. The solvents were p.a. grade for the reaction mixtures and industrial grade for the flash column chromatography. Analytical TLC was performed on silica gel coated alumina plates (MN TLC sheets ALUGRAM® Xtra SIL G/UV254). The visualization was performed using UV-light (254 and 366 nm). UV–Vis analyses were performed with Varian Cary 50 UV/Vis spectrophotometer and Agilent 8453 UV-Vis Spectrometer. For UV measurements 10 mm Hellma fluorescence quartz cuvettes (117.100F-QS) with a screw cap with PTFE-coated silicon septum were used. Irradiation Source: Philips LUXEON® Rebel (purple, max = 400 ± 10 nm, 1000 mA, 1.2 W). Chalcone **1i** was purchased from Sigma-Aldrich.

General procedure for preparation of α,β-unsaturated ketones 1a-1h and 1j-1n. Synthetic procedures and chemical characterizations are available in the Supporting Information.

General procedure for the photo rearrangement/addition reaction. In a 5 mL snap vial equipped with magnetic stirring bar the PPh_3 (0.5 equiv, 0.125 mmol) and aryl chalcone derivatives (1.0 equiv, 0.25 mmol) were added in 1 mL of CH_3OH, and the resulting reaction mixture was degassed by three “pump-freeze-thaw” cycles via a syringe needle. The vial was irradiated through the vial’s plane bottom side using 400 nm purple LEDs with cooling device maintaining a temperature around 20 °C. After 20h of irradiation, the solvent was removed and purified by flash column chromatography using petrol ether/ethyl acetate (99:1 to 99:5) as eluent.

3-Methoxy-2-phenyl-1-(thiophen-2-yl)propan-1-one (2a). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (dd, *J* = 3.8, 1.1 Hz, 1H), 7.61 – 7.57 (m, 1H), 7.39 – 7.34 (m, 2H), 7.32 (ddd, *J* = 7.6, 4.5, 1.2 Hz, 2H), 7.06 (dd, *J* = 4.9, 3.9 Hz, 1H), 4.71 (dd, *J* = 8.9, 5.3 Hz, 1H), 4.18 (t, *J* = 9.0 Hz, 1H), 3.64 (dd, *J* = 9.1, 5.3 Hz, 1H), 3.36 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.1, 144.1, 136.3, 134.0, 132.7, 129.0, 128.3, 128.1, 127.7, 74.4, 59.2, 55.3. HRMS (ESI) calcd for $C_{14}H_{14}O_2S$ $[M + H]^+$ 247.0787 found 247.0788.

2-(4-Fluorophenyl)-3-methoxy-1-(thiophen-2-yl)propan-1-one (2b). Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.74 (dd, *J* = 3.8, 1.1 Hz, 1H), 7.63 – 7.59 (m, 1H), 7.37 – 7.30 (m, 2H), 7.07 (dt, *J* = 7.3, 3.6 Hz, 1H), 7.04 – 6.96 (m, 2H), 4.73 – 4.66 (m, 1H), 4.13 (t, *J* = 8.9 Hz, 1H), 3.62 (dd, *J* = 9.1, 5.5 Hz, 1H), 3.35 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.1, 143.8, 134.3, 132.7, 129.9, 129.8, 128.2, 116.1, 115.8, 74.3, 59.2, 54.3. HRMS (ESI) calcd for $C_{14}H_{13}FO_2S$ $[M + H]^+$ 265.0693 found 265.0696.

2-(4-Bromophenyl)-3-methoxy-1-(thiophen-2-yl)propan-1-one (2c). Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.72 (dd, *J* = 3.8, 1.1 Hz, 1H), 7.60 (dd, *J* = 4.9, 1.1 Hz, 1H), 7.46 – 7.40 (m, 2H), 7.27 – 7.22 (m, 2H), 7.06 (dd, *J* = 4.9, 3.9 Hz, 1H), 4.67 (dd, *J* = 8.5, 5.7 Hz, 1H), 4.20 – 4.03 (m, 1H), 3.62 (dd, *J* = 9.1, 5.7 Hz, 1H), 3.34 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 190.7, 143.7, 135.4, 134.5, 132.8, 132.1, 130.0, 128.3, 121.8, 74.1, 59.3, 54.5. HRMS (ESI) calcd for $C_{14}H_{13}BrO_2S$ $[M + H]^+$ 324.9892 found 324.9894.

2-(4-Chlorophenyl)-3-methoxy-1-(thiophen-2-yl)propan-1-one (2d). Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.77 – 7.69 (m, 1H), 7.65 – 7.54 (m, 1H), 7.29 (d, *J* = 2.1 Hz, 3H), 7.12 – 6.98 (m, 1H), 4.68 (dd, *J* = 9.1, 5.7 Hz, 1H), 4.19 – 4.03 (m, 1H), 3.62 (dd, *J* = 9.1, 5.7 Hz, 1H), 3.34 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 190.8, 143.7, 134.8, 134.4, 133.7, 132.8, 129.6, 129.2, 128.3, 74.2, 59.3, 54.5. HRMS (ESI) calcd for $C_{14}H_{13}ClO_2S$ $[M + H]^+$ calcd for 281.0398 found 281.0398.

2-(3-Bromophenyl)-3-methoxy-1-(thiophen-2-yl)propan-1-one (2e). Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.74 (dd, *J* = 3.8, 1.0 Hz, 1H), 7.62 (dd, *J* = 4.9, 1.0 Hz, 1H), 7.53 (dd, *J* = 6.4, 4.7 Hz, 1H), 7.41 – 7.34 (m, 1H), 7.34 – 7.28 (m, 1H), 7.23 – 7.16 (m, 1H), 7.11 – 7.04 (m, 1H), 4.67 (dd, *J* = 8.6, 5.6 Hz, 1H), 4.17 – 4.08 (m, 1H), 3.63 (dd, *J* = 9.1, 5.6 Hz, 1H), 3.34 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 190.5, 143.8, 138.5, 134.6, 132.9, 131.3, 130.9, 130.5, 128.3, 127.0, 123.0, 74.2, 59.3, 54.7. HRMS (ESI) calcd for $C_{14}H_{13}BrO_2S$ $[M + H]^+$ calcd for 324.9892 found 324.9891.

3-Methoxy-1-(thiophen-2-yl)-2-(p-tolyl)propan-1-one (2f). Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75 (dd, *J* = 3.8, 0.9 Hz, 1H), 7.54 (dd, *J* = 4.9, 0.9 Hz, 1H), 7.28 (s, 1H), 7.12 (d, *J* = 8.0 Hz, 2H), 7.03 (dd, *J* = 4.9, 3.9 Hz, 1H), 4.71 (dd, *J* = 8.9, 5.3 Hz, 1H), 4.22 – 4.13 (m, 1H), 3.62 (dd, *J* = 9.1, 5.3 Hz, 1H), 3.35 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.3, 144.1, 137.4, 134.0, 133.3, 132.7, 129.7, 128.2, 74.4, 59.2, 54.8, 21.1. HRMS (ESI) calcd for $C_{15}H_{16}O_2S$ $[M + H]^+$ 261.0944 found 261.0946.

3-Methoxy-1,2-diphenylpropan-1-one (2i). Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.02 – 7.95 (m, 2H), 7.50 – 7.45 (m, 1H), 7.43 – 7.37 (m, 2H), 7.32 (dt, *J* = 8.7, 1.7 Hz, 4H), 7.25 – 7.21 (m, 1H), 4.90 (dd, *J* = 8.7, 5.3 Hz, 1H), 4.25 – 4.14 (m, 1H), 3.65 (dd, *J* = 9.1, 5.3 Hz, 1H), 3.36 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.3, 136.7, 136.3, 133.1, 129.0, 128.8, 128.6, 128.4, 127.6, 74.7, 59.2, 53.8. HRMS (ESI) calcd for $C_{16}H_{16}O_2$ $[M + H]^+$ calcd for 241.1223 found 241.1228.

3-Methoxy-1-phenyl-2-(p-tolyl)propan-1-one (2j). Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.04 – 7.94 (m, 2H), 7.49 – 7.45 (m, 1H), 7.41-7.29 (m, 2H), 7.23 (d, *J* = 8.1 Hz, 2H), 7.12 (d, *J* = 7.9 Hz, 2H), 4.87 (dd, *J* = 8.7, 5.3 Hz, 1H), 4.18 (t, *J* = 8.9 Hz, 1H), 3.63 (dt, *J* = 11.1, 5.5 Hz, 1H), 3.36 (s, 3H), 2.29 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.4, 137.3, 136.7, 133.3, 133.0, 129.8, 128.8, 128.5, 128.2, 74.7, 59.2, 53.4, 21.1. HRMS (ESI) calcd for $C_{17}H_{18}O_2$ $[M + H]^+$ 255.1380, found 255.1377.

3-Methoxy-1-(naphthalen-2-yl)-2-phenylpropan-1-one (2n). Colorless solid. ^1H NMR (300 MHz, $CDCl_3$) δ 8.51 (s, 1H), 8.04 (dd, *J* = 8.7, 1.8 Hz, 1H), 7.92 (d, *J* = 7.9 Hz, 1H), 7.82 (dd, *J* = 12.2, 6.8 Hz, 2H), 7.54 (ddd, *J* = 9.2, 5.1, 1.4 Hz, 2H), 7.41-7.38 (m, 2H), 7.34 – 7.28 (m, 2H), 7.25 – 7.21 (m, 1H), 5.06 (dd, *J* = 8.7, 5.3 Hz, 1H), 4.25 (t, *J* = 8.9 Hz, 1H), 3.71 (dd, *J* = 9.1, 5.3 Hz, 1H), 3.38 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.3, 136.5, 135.5, 134.1, 132.4, 130.6, 129.7, 129.1, 128.5, 128.4, 127.7, 127.6, 126.7, 124.4, 74.8, 59.2, 53.8. HRMS (ESI) calcd for $C_{20}H_{18}O_2$ $[M + H]^+$ 291.1380 found 291.1381.

Synthesis of the 2-substituted terminal enone 8. To 3-methoxy-1,2-diphenylpropan-1-one (0.10 g, 0.83 mmol) in 2 ml of toluene was added sodium methoxide (1.0 mg, 0.019 mmol). The mixture was heated to 160-170 °C for 1.5 h. The solvent was evaporated and the residue was purified by flash column chromatography using petrol ether/ethyl acetate (50:1) as eluent. White solid. ^1H NMR (300 MHz, $CDCl_3$) δ 7.95 – 7.86 (m, 2H), 7.60 – 7.32 (m, 8H), 6.08 (s, 1H), 5.65 (s, 1H). The spectroscopy is in accordance with literature.[23]

Conclusions

In conclusion, we have reported the rearrangement and methanol addition reaction of aryl chalcones mediated by PPh_3 under UV-A irradiation. The reaction proceeds smoothly at room temperature without sensitizers using 400 nm emitting LEDs. The rearrangement product can be further converted into 2-substituted terminal enones, which are interesting molecular structures with potential biologically activity. We propose two possible mechanistic hypotheses for this rearrangement/addition reaction either involving the formation of a phosphine-carbonyl intermediate, nucleophilic addition of MeOH and 1, 2 aryl migration or reaction *via* ylide and carbene intermediates.

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Notes and references

[a] *Institute of Organic Chemistry, University of Regensburg, Universitätstr. 31, 93053 Regensburg, Germany. E-mail: Burkhard.Koenig@ur.de*

[b] *Beijing National Laboratory for Molecular Sciences, CAS Key Laboratory of Photochemistry, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, People's Republic of China*

†Electronic Supplementary Information (ESI) available: characterization details with NMR spectra and UV-vis spectra for supplementary information. Details of the crystal structure analysis of compound **2n** have been deposited with the Cambridge Crystallographic Structure data base and can be obtained free of charge; deposition number: CCDC 1041821.

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