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A triphenylphosphine mediated photo-rearrangement and methanol addition of aryl chalcones to 1-propanones†

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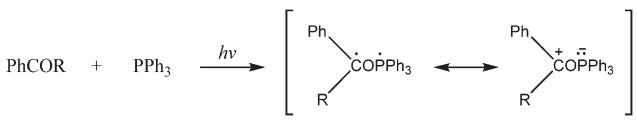
Aryl chalcones rearrange and add methanol to give substituted propane-1-ones upon UV-A irradiation in the presence of PPh_3. We propose two possible mechanisms for this photo-rearrangement. The reaction involves either the formation of a phosphine-carbonyl intermediate, nucleophilic addition of MeOH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

Introduction

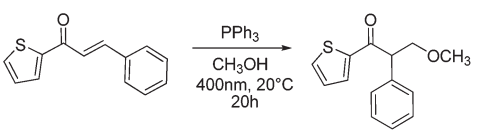
The photochemistry of chalcones has always attracted the interest of organic chemists. In recent years, the reactions of aryl enones under visible light photoredox catalysis have been studied.[1–10] Typical reaction conditions use a ruthenium complex as a visible light absorbing photoredox catalyst and a tertiary amine as a sacrificial electron donor to initiate a photoinduced electron transfer that reduces the enone to its corresponding radical anion, which undergoes an inter- or intra-molecular [2 + 2] cycloaddition[4,7] or a reductive coupling.[9] The photochemistry of aryl ketones in the presence of PPh_3 was studied more than 40 years ago,[11–14] but the investigations were 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 cyclization of enones, where 9,10-dicyanoanthracene (DCA) was employed as photoredox catalyst and PPh_3 as the sacrificial electron donor.[16] In addition to its role as an electron donor similar to tertiary amines, PPh_3 has some unique properties: it is sterically more hindered; it has no hydrogen atom donor and it is an efficient quencher of the carbonyl triplet state (Scheme 1). Therefore,



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

the photochemical behavior of α,β-unsaturated ketones in the presence of PPh_3 grabbed our interest.

We investigated the photoreaction of a variety of chalcone derivatives in the presence of PPh_3 using different solvents, catalysts and light sources. The reaction of chalcone **1a** with 10 mol% of DCA and PPh_3 (1 equiv.) in MeOH after 20 h of 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 the 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 *via* oxidative processes.[19] However, since PPh_3 is not an oxidative reagent, we propose a different mechanism and developed a convenient experimental procedure for this interesting rearrangement.



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

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†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**. CCDC 1041821. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5pp00009b

Results and discussion

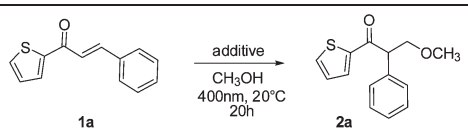
Initially, the required amount of PPh_3 for the photoreaction was investigated (Table 1). The desired product was obtained in 84% yield with 0.5 equiv. of PPh_3. Decreasing the amount of PPh_3 to 0.25 equiv. does not reduce the product yield, but with catalytic amounts of less than 10 mol% PPh_3, the yield of the reaction dropped to 28%. During work up, 30%–40% of the PPh_3 could be recycled by column chromatography. Triphenylphosphine oxide was isolated as a by-product. 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 ESI†). Control experiments without PPh_3, without light or under reflux conditions gave no product, revealing that PPh_3 and light were essential (entries 8, 9 and 10). MeOH was replaced with EtOH, i-PrOH or CF_3CH_2OH but no product formation was detected in these solvents by GC-MS analysis of the reaction mixture. Moreover, the reaction was also carried out with photosensitizers, *e.g.*, $Ru(bpy)_3Cl_2{\cdot}6H_2O$ and Eosin Y, at 450 nm and 530 nm, respectively. The formation of the [2 + 2] cycloaddition product and a reductive coupling product were observed when $Ru(bpy)_3Cl_2{\cdot}6H_2O$ was used in the reaction, while no reaction occurred when it was irradiated with Eosin Y at 530 nm.

Next, we investigated the substrate scope of the aryl chalcones in the photoreaction, and the results are summarized in Table 2. Phenyl and naphthyl chalcones rearrange using the abovementioned reaction conditions. The X-ray structure analysis of compound **2n** confirmed the structure of the molecule (Fig. 1). Chalcones bearing moderate electron-withdrawing, neutral and electron-donating substituents reacted smoothly to afford the corresponding products in moderate to good yield. Strong electron-withdrawing and electron-donating substituents such as –OCH_3, –NO_2 and –CN on either of the aromatic rings inhibit the rearrangement reaction; the products of the [2 + 2] cycloaddition were observed in these cases (see ESI†).

Several reactions were performed to investigate the mechanism of the photorearrangement/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 was fully deuterated, while the less reactive β-hydrogen atoms were not completely exchanged by deuterium.

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 the related

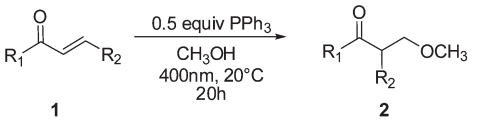
Table 1 Investigation of different reaction conditions for the photorearrangement/addition reaction of **1a**



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 a N_2 atmosphere.

Table 2 Scope of aryl chalcones in the photorearrangement/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 a N_2 atmosphere.

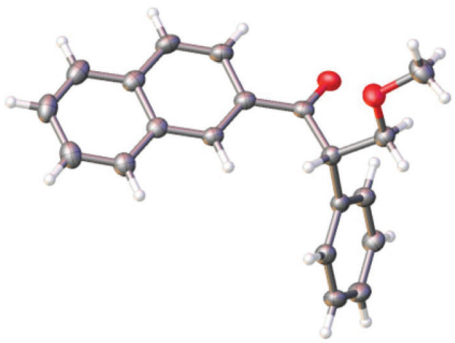
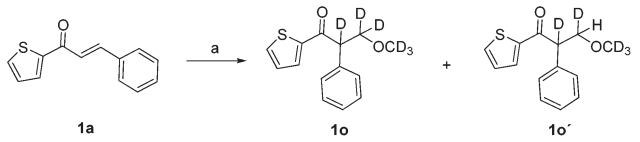
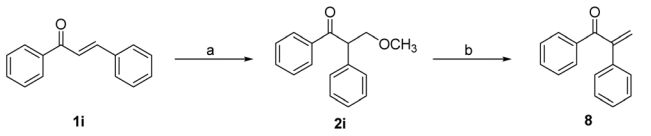


Fig. 1 Structure of compound **2n** in the solid state obtained from the photorearrangement/addition reaction of aryl chalcone **1n**.

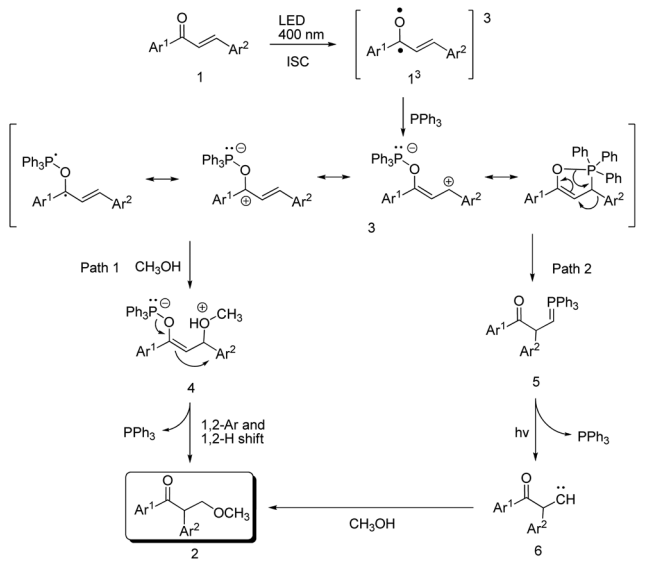


Scheme 3 The photorearrangement/addition reaction of **1a** in CD_3OD leads to deuterium incorporation. Reaction conditions: (a) 0.5 equiv. PPh_3, CD_3OD, 20 °C, 20 h.



Scheme 5 Synthesis of the 2-substituted terminal enone **8** using the PPh_3 mediated photorearrangement/addition reaction of compound **1i** and the subsequent elimination of methanol. Reaction conditions: (a) 0.5 equiv. PPh_3, CH_3OH, 20 °C, 20 h, 78%. (b) 1% $NaOCH_3$, $PhCH_3$, 160–170 °C, 1.5 h, 72%.

reports,[14,15,20] we propose two possible mechanisms shown in Scheme 4. Photochemical excitation of the α,β-unsaturated ketone **1** and ISC gives its triplet state **1**,[3] which is captured by PPh_3 to form **3** through the intervention of an exciplex. The electronic structure of compound **3** is described by four resonance structures. In pathway 1, compound **3** undergoes nucleophilic attack by MeOH to give the intermediate **4**. A 1,2-aryl shift and 1,2-hydrogen shift provide product **2** of the rearrangement addition reaction sequence. In pathway 2, a 1,2-aryl migration occurs, giving the 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 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 give 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 The suggested mechanistic hypothesis for the photorearrangement/addition reaction of aryl chalcones in the presence of PPh_3.

To demonstrate its synthetic application, we used the photoreaction product **2i** in the synthesis of the 2-substituted enone **8** (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 the standard photoreaction conditions provided the corresponding product **2i**, which was then further converted into 1,2-diphenylprop-2-en-1-one **8** upon heating to 160–170 °C with 1% $NaOCH_3$ in toluene.[22]

Experimental

General

^1H and ^{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) and a Bruker AVANCE 400 spectrometer (operating at 400.13 MHz for ^1H and 100.62 MHz for ^{13}C), respectively. The spectra were obtained using chloroform-d (99.8%, Deutero GmbH) and referenced against the non-deuterated (^1H)/deuterated (^{13}C) solvents. The shift values (δ H and δ C) are reported in ppm with J values in Hz. The melting points were measured using a Stanford Research Systems OptiMelt MPA 100. The high resolution 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 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 flash column chromatography. Analytical TLC was performed on silica gel coated alumina plates (MN TLC sheets ALUGRAM® Xtra SIL G/UV254). 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 and 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 the preparation of α,β-unsaturated ketones 1a–1h and 1j–1n. Synthetic procedures and chemical characterizations are available in the ESI.†

General procedure for the photorearrangement/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 derivative (1.0 equiv., 0.25 mmol) were added in 1 mL of CH_3OH and the resulting reaction mixture was degassed *via* three "pump–freeze–thaw" cycles using a syringe needle. The vial was irradiated through the vial's plane bottom side using 400 nm purple LEDs with a cooling device, maintaining the reaction temperature at around 20 °C. After 20 h of irradiation, the solvent was removed and the residue purified by flash column chromatography using petroleum ether–ethyl acetate (99 : 1 to 99 : 5) as the 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. ^{1}H 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. Sodium methoxide (1.0 mg, 0.019 mmol) to 3-methoxy-1,2-diphenylpropan-1-one (0.10 g, 0.83 mmol) in 2 mL of toluene. The mixture was heated to 160–170 °C for 1.5 h. The solvent was evaporated and the residue purified by flash column chromatography using petroleum ether–ethyl acetate (50 : 1) as the eluent. White solid. ^{1}H 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 spectra was in accordance with that reported in the literature.[23]

Conclusions

In conclusion, we have reported the photorearrangement and methanol addition reaction of aryl chalcones mediated by PPh_3 under UV-A irradiation. The reaction proceeds smoothly at room temperature without the presence of a sensitizer using

400 nm emitting LEDs. The rearrangement product can be further converted into 2-substituted terminal enones, which are interesting molecular structures with potential biological activity. We propose two possible mechanistic hypotheses for this rearrangement/addition reaction, involving either the formation of a phosphine-carbonyl intermediate, nucleophilic addition of MeOH and 1,2-aryl migration or reaction *via* ylide and carbene intermediates.

Acknowledgements

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