A novel method of remotely triggering a cyclopropyl carbinyl to homo-allyl radical fragmentation process

Clive S. Penkett* and Richard Lane

Department of Chemistry, University of Sussex, Brighton BN1 9QJ, UK

A series of model compounds were prepared in order to investigate the conditions that would favour the formation of a cyclopropyl carbinyl radical *via* a 1,5 hydrogen atom translocation process. The models varied in the degree of unsaturation adjacent to the cyclopropyl carbinyl position and it was found that the 1,5 hydrogen atom radical translocation process was favoured only when alternative cyclisation pathways were not possible.

Keywords: 1,5-hydrogen atom translocation, radical cyclisation, cyclopropyl carbinyl radical fragmentation

The remote functionalisation of carbon atoms is a very powerful technique, as it allows an apparently unactivated C–H bond to be broken and the resulting carbon-centred radical can then undergo various bond-forming processes. One of the first examples of this methodology was reported by Hofmann in the late nineteenth century and later became known as the Hofmann–Löffler–Freytag reaction.[1] Many notable contributions have subsequently been made to this field by Barton,[2] Breslow,[3] Curran,[4] Parsons,[5] De Mesmaeker,[6] Murphy,[7] Rawal[8] as well as others.[4]

One of the great challenges facing a radical chemist is to selectively direct a newly created radical down a particular reaction pathway and away from all the other possibilities available to it. Ring forming reactions of carbon-centred radicals are very common, but ring fragmentation reactions are generally unfavourable and not often employed in organic synthesis. One exception to this is the cyclopropyl carbinyl to homo-allyl radical rearrangement,[9] which is both fast and thermodynamically favourable. We were interested in developing a system whereby the formation of a cyclopropyl carbinyl radical could be triggered remotely *via* a 1,5 hydrogen atom translocation process.

To investigate this chemical methodology, a model system (Fig. 1) was designed which would generate a high energy vinyl radical 5-atom-positions away from the cyclopropyl carbinyl hydrogen atom and could be easily modified to allow for a variation in the degree of unsaturation adjacent to the cyclopropyl carbinyl position.

Three examples of the model system (**2**, **6** and **11**) were prepared with either an alkyne, an alkene or an alkane group appended to the cyclopropyl carbinyl position. Each was generated from the substituted cyclopropyl carbinol derivatives **1**,[10] **5**[11] and **8**[12] respectively by conversion to an appropriate ether. In attempting to alkylate the various secondary alcohols (**1**, **5** and **8**), we found that as the degree of unsaturation adjacent to the hydroxyl group decreased, so did the ease with which it could be alkylated with 1,3-dibromopropene. Alcohols **1** and **5** were converted to bromo ethers **2** and **6** by reaction with 1,3-dibromopropene under phase transfer conditions. Unfortunately alcohol **8** failed to react with 1,3-dibromopropene under phase transfer conditions or by using sodium hydride as a base. It could, however, be converted to the propargyl ether **9** with propargyl bromide under phase transfer conditions, then hydro-stannylated[13] and converted to the alkenyl iodide **11**. With the three examples (**2**, **6** and **11**) in hand, each was subjected to radical forming conditions using a mixture of tributyltin hydride and a substoichiometric amount of AIBN (Scheme 1).

When the alkynyl compound **2** was heated together with tributyltin hydride and AIBN in benzene, two new compounds (**3** and **4**) were isolated. The minor component was only

* Correspondent. E-mail: c.s.penkett@sussex.ac.uk

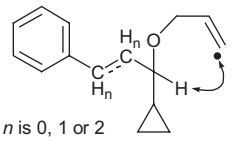
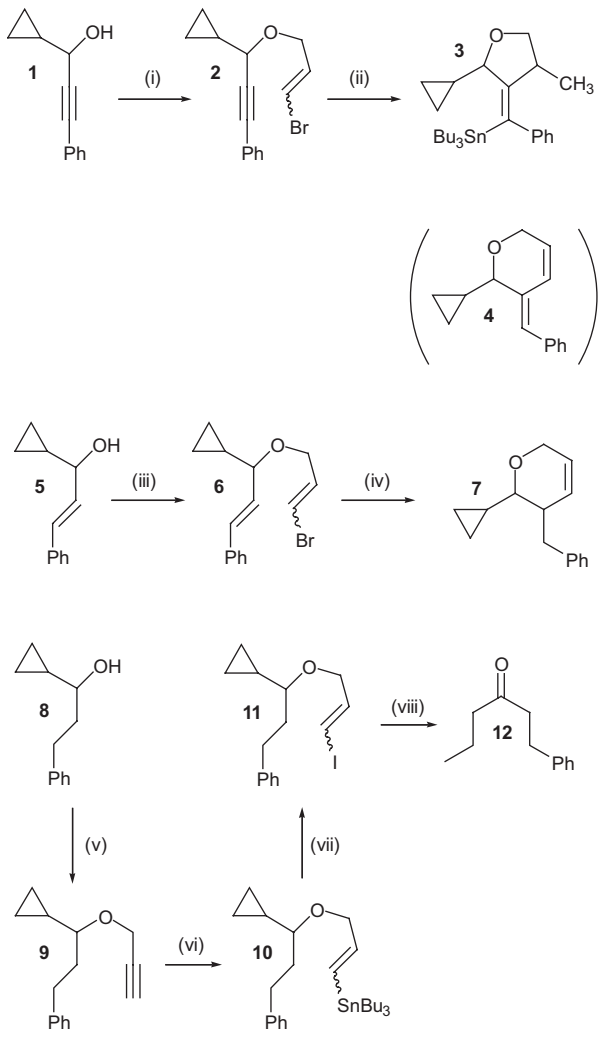


Fig 1.



Scheme 1 *Reagents and conditions:* (i) $NaOH_{(aq)}/CH_2Cl_2$, CTAB,[14] 1,3-dibromopropene, 77%; (ii) 1.3 eq. Bu_3SnH, 20 h, 0.1 eq. AIBN, PhH (0.02 M), Δ, 27%; (iii) $NaOH_{(aq)}/CH_2Cl_2$, CTAB,[14] 1,3-dibromopropene, 44%; (iv) 1.3 eq. Bu_3SnH (4 h via syringe pump), 0.1 eq. AIBN, PhH (0.02 M), Δ, 46%; (v) $NaOH_{(aq)}/CH_2Cl_2$, CTAB,[14] propargyl bromide, 23%; (vi) Bu_3SnH, AIBN, PhH, Δ, 64%; (vii) I_2, CH_2Cl_2, 81%; (viii) 1.3 eq. Bu_3SnH (20 h via syringe pump), 0.1 eq. AIBN, PhH (0.02 M), Δ, 33%.

obtained in a trace amount and tentatively assigned the structure **4**. This would have been formed as a result of bromine abstraction from the alkenyl bromide and the resulting radical undergoing 6-*exo-dig* cyclisation onto the alkyne. The major component (**3**) was formed as a result of rapid stannyl radical addition to the alkyne, followed by 5-*exo-trig* cyclisation[15] onto the alkenyl bromide moiety and hydride abstraction from tin hydride. The resulting alkyl bromide was then reduced by another equivalent of tributyltin hydride to afford compound **3**. This is very interesting, because the occurrence of **3** rather than **4** as the major product shows that the rate of bromine abstraction from the alkenyl bromide of **2** is slower than the rate of tin radical addition to the alkyne moiety. Crich[16] has shown in a related system that the opposite is also true (Scheme 2), suggesting that there is a fairly fine balance between steric and electronic effects controlling the behaviour of the tin radical.

For the second example a solution of tributyltin hydride and AIBN was added *via* a syringe pump to a solution of the alkenyl compound **6** in benzene. After bromine abstraction the resulting alkenyl radical underwent a 6-*exo-trig* cyclisation reaction onto the alkene of the allylic ether and was subsequently reduced to afford compound **7**.

For the final example a solution of tributyltin hydride and AIBN was added *via* a syringe pump to a solution of the alkyl compound **11** in benzene. The only isolatable product obtained from this reaction was ketone **12**. This had presumably formed as a result of the initially formed alkenyl radical undergoing a 1,5-hydrogen atom translocation step to form a cyclopropyl carbinyl radical, which then triggered the fragmentation of the strained three membered ring to give a homo-allylic radical. This abstracted a hydrogen atom from tin hydride to form an enol ether, which was then hydrolysed during the work-up procedure to afford the ketone product **12** (Scheme 3).

In conclusion we have shown that, given the correct set of circumstances, remote activation of a cyclopropyl carbinyl position is possible using a 1,5 hydrogen atom abstraction process. This remote activation method is only possible however if alternative favourable cyclisation processes are not available to the initially formed radical.

Experimental

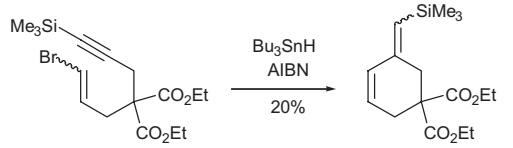
When an inseparable mixture of isomers was obtained, the ^{13}C signals for both compounds are reported.

[3-(3-Bromoallyloxy)-3-cyclopropylprop-1-ynyl]-benzene (**2**): To a stirred solution of 1-cyclopropyl-3-phenylprop-2-yn-1-ol **1**[10] (0.77 g, 4.49 mmol) in dichloromethane (10 cm^3) was added cetyltrimethylammonium bromide (0.24 g, 0.67 mmol) and NaOH (50% aqueous solution) (10 cm^3). After stirring at room temperature for 1.5 h, (*E,Z*) 1,3-dibromopropene (1.08 g, 5.4 mmol) was added dropwise and the reaction mixture stirred for 1 h. The reaction mixture was diluted with water (20 cm^3), the aqueous layer was separated and extracted with dichloromethane (3 × 20 cm^3). The combined organic layers were dried ($MgSO_4$), concentrated *in vacuo* and purified by flash chromatography (silica, 2% Et_2O in petrol) to give a (1 : 1) mixture of *E* and *Z* bromoalkenes **2** (1.02 g, 77%) as a colourless oil; R_F = 0.90 (10% EtOAc in petrol); υ_{max} (thin film)/cm^{-1} 3083, 3008, 2227, 1626, 1598; ^1H NMR (300 MHz, $CDCl_3$) δ 0.40–0.65 (m, 4H), 1.25–1.35 (m, 1H), 4.07 (ddd, *J* = 0.6, 6.1, 12.9, 0.5H), 4.19 (d, *J* = 6.4, 0.5H), 4.21 (d, *J* = 6.4, 0.5H), 4.28 (ddd, J = 1.1, 5.3, 12.9, 0.5H), 4.35 (ddd, *J* = 1.4, 5.7, 12.9, 0.5H), 4.47 (ddd, *J* = 1.5, 4.8, 12.9, 0.5H), 6.30–6.45 (m, 2H), 7.30–7.50 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 1.97, (3.15 + 3.22), 14.96, (66.50 + 67.93), (72.77 + 73.24), (85.44 + 85.60), (86.26 + 86.34), (109.03 + 109.36), (122.36 + 122.50), (128.24 + 128.27), (128.41 + 128.49), 131.78, (132.02 + 133.93); *m/z* (EI-MS) 291 ([M(^{81}Br)–H]$^+$, 3%), 289 ([M(^{79}Br)–H]$^+$, 2%), 211 ([M–Br]$^+$, 37%), 141 (100%); HRMS predicted for [M–Br] $C_{15}H_{15}O$ 211.1123, found 211.1131.

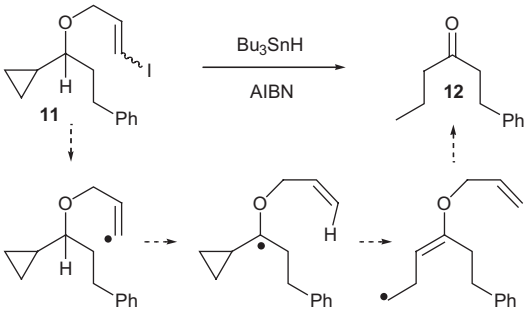
Tri-n-butyl-[(2-cyclopropyl-4-methyl-dihydro-furan-3-ylidene)-phenyl-methyl]-stannane (**3**): To a degassed solution of the alkenyl bromide **2** (0.02 M) (200 mg, 0.68 mmol) in benzene (34 cm^3) was added tributyltin hydride (0.24 cm^3, 0.89 mmol) and AIBN (11 mg, 0.07 mmol) and the reaction mixture was heated at reflux for 20 h. The solution was cooled and added to NH_4OH (20% aqueous solution) (25 cm^3) and stirred for 24 h. The aqueous layer was separated and extracted with EtOAc (3 × 30 cm^3). The combined organic layers were dried ($MgSO_4$), concentrated *in vacuo* and purified by flash chromatography (silica, 100% petrol then 2% Et_2O in petrol) to give an inseparable mixture of isomers of the stannane **3** (93 mg, 27%)) as a yellow oil and and starting material **2** (20 mg, 16%); R_F = 0.45 (5% EtOAc in petrol); υ_{max} (thin film)/cm^{-1} 3079, 3010, 2956, 2871, 1654; ^1H NMR (300 MHz, $CDCl_3$) δ 0.40–0.60 (m, 10H), 0.80–0.90 (m, 1H), 0.83 (t, *J* = 7.1, 9H), 0.94 (d, *J* = 7.0, 1.65H), 1.02 (d, *J* = 7.1, 1.35H), 1.10–1.40 (m, 12H), 2.25–2.35 (m, 0.45H), 2.50–2.60 (m, 0.55H), 3.46 (dd, *J* = 4.6, 11.0, 0.45H), 3.70–3.80 (m, 1.55H), 3.91 (dd, *J* = 2.2, 6.8, 0.55H), 4.08 (dd, *J* = 4.2, 11.0, 0.45H), 7.05–7.35 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (1.97 + 2.63), (3.91 + 6.34), (11.00 + 11.08), 13.63, (16.24 + 17.01), (17.28 + 17.71), 27.33, 29.12, (36.21 + 36.45), (67.36 + 68.87), (80.35 + 80.72), (126.72 + 127.15), (127.84 + 128.14), (128.46 + 129.23), (140.52 + 141.11), (144.18 + 144.81), (150.66 + 151.20); ; *m/z* (EI-MS) 451 ([M(^{124}Sn)–Bu]$^+$, 15%), 449 ([M(^{122}Sn)–Bu]$^+$, 20%), 448 ([M(^{121}Sn)–Bu]$^+$, 30%), 447 ([M(^{120}Sn)–Bu]$^+$, 100%), 446 ([M(^{119}Sn)–Bu]$^+$, 55%), 445 ([M(^{118}Sn)–Bu]$^+$, 85%), 444 ([M(^{117}Sn)–Bu]$^+$, 45%), 443 ([M(^{116}Sn)–Bu]$^+$, 55%), 213 ([M–$SnBu_3$]$^+$, 30%); HRMS predicted for $C_{23}H_{35}O^{120}Sn$ 447.1709, found 447.1842. (There were problems making the accurate mass measurement due to the presence of the multiple tin isotopes).

[3-(3-Bromoallyloxy)-3-cyclopropylpropenyl]-benzene (**6**): To a stirred solution of 1-cyclopropyl-3-phenylprop-2-en-1-ol **5**[11] (0.56 g, 3.20 mmol) in dichloromethane (10 cm^3) was added cetyltrimethylammonium bromide (0.18 g, 0.48 mmol) and NaOH (50% aqueous solution) (10 cm^3). After stirring at room temperature for 1.5 h, (*E,Z*) 1,3-dibromopropene (0.77 g, 3.80 mmol) was added dropwise and the reaction mixture stirred for 24 h. The reaction mixture was diluted with water (20 cm^3) and the aqueous layer was separated and extracted with dichloromethane (3 × 20 cm^3). The combined organic layers were dried ($MgSO_4$), concentrated *in vacuo* and purified by flash chromatography (silica, 10% Et_2O in petrol) to give a mixture of *E* and *Z* bromoalkenes **5** (0.42 g, 44%) as a yellow oil; R_F = 0.85 (10% EtOAc in petrol); υ_{max} (thin film)/cm^{-1} 3081, 3006, 2853, 1626, 1620; ^1H NMR (300 MHz, $CDCl_3$) δ 0.20–0.70 (m, 4H), 1.00–1.15 (m, 1H), 3.85–4.25 (m, 3H), 6.10–6.60 (m, 4H), 7.15–7.50 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (1.71 + 1.80), (3.93 + 3.98), (15.38 + 15.62), (66.15 + 67.96), (84.00 + 84.32), (108.25 + 108.94), (126.50 + 126.55), (127.71 + 127.81), (128.56 + 128.60), (128.77 + 128.80), (132.08 + 132.17), (132.60 + 134.53), (136.42 + 136.42); *m/z* (EI–MS) 294 (M$^+$(^{81}Br), 4%), 292 (M$^+$(^{79}Br), 4%), 213 ([M–Br]$^+$, 22%), 69 (100); HRMS predicted for [M–Br] $C_{15}H_{17}O$ 213.1279, found 213.1279.

3-Benzyl-2-cyclopropyl-3,6-dihydro-2H-pyran (**7**): To a degassed solution of the alkenyl bromide **6** (0.02 M) (100 mg, 0.34 mmol) in benzene (17 cm^3) was added AIBN (6 mg, 0.04 mmol). The solution was heated to reflux under an atmosphere of nitrogen, whereupon a solution of tributyltin hydride (0.13 cm^3, 0.44 mmol) and AIBN



Scheme 2



Scheme 3

(6 mg, 0.04 mmol) in benzene (5 cm^3) was added *via* a syringe pump over 4 h. After addition was complete, the solution was maintained at reflux for a further 16 h. To the cooled solution was added NH_4OH (30% aqueous solution) (15 cm^3) and stirred for 24 h. The aqueous layer was separated and extracted with EtOAc (3 × 20 cm^3). The combined organic layers were dried ($MgSO_4$), concentrated *in vacuo* and purified by flash chromatography (silica, 100% petrol then 5% Et_2O in petrol) to give the cyclic ether **7** (33 mg, 46%) as a yellow oil and a trace of starting material; R_F = 0.30 (10% Et_2O in petrol); υ_{max} (thin film)/cm^{-1} 3082, 3027, 2926, 2824, 1650, 1603; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.20–0.40 (m, 2H), 0.50–0.70 (m, 2H), 0.95–1.10 (m, 1H), 2.38 (dd, *J* = 9.6, 13.5, 1H), 2.50–2.65 (m, 2H), 3.12 (dd, *J* = 4.9, 13.5, 1H), 4.11 (br d, *J* = 16.6, 1H), 4.24 (br d, *J* = 16.6, 1H), 5.61 (ddd, *J* = 2.2, 4.2, 10.3, 1H), 5.72 (ddt, *J* = 2.0, 4.6, 10.3, 1H), 7.12–7.30 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 1.83, 4.12, 14.13, 38.34, 42.05, 64.63, 81.94, 125.88, 125.97, 127.41, 128.30, 129.22, 139.79; *m/z* (EI–MS) 214 (M^+, 32%), 144 (98%), 129 (100%); HRMS predicted for $C_{15}H_{18}O$ 214.1357, found 214.1350.

(3-Cyclopropyl-3-prop-2-ynyloxypropyl)-benzene (**9**): To a stirred solution of 1-cyclopropyl-3-phenylpropan-1-ol **8**[12] (3.84 g, 21.8 mmol) in dichloromethane (25 cm^3) was added cetyltrimethylammonium bromide (1.43 g, 3.93 mmol) and NaOH (50% aqueous solution) (25 cm^3). After stirring at room temperature for 1.5 h, propargyl bromide (80% weight in toluene) (3.11 g, 3.80 mmol) was added dropwise and the reaction mixture stirred for 60 h. The reaction mixture was diluted with water (50 cm^3) and the aqueous layer was separated and extracted with dichloromethane (3 × 20 cm^3). The combined organic layers were dried ($MgSO_4$), concentrated *in vacuo* and purified by flash chromatography (silica, 5% Et_2O in petrol) to give (3-cyclopropyl-3-prop-2-ynyloxypropyl)-benzene **9** (1.06 g, 23%) as a yellow oil; R_F = 0.90 (10% EtOAc in petrol); υ_{max} (thin film)/cm^{-1} 3300, 3081, 3003, 2927, 2861, 2115, 1604; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.00–0.10 (m, 1H), 0.38–0.50 (m, 2H), 0.60–0.65 (m, 1H), 0.78–0.90 (m, 1H), 1.90–2.00 (m, 2H), 2.39 (s, 1H), 2.60–2.85 (m, 3H), 4.30–4.35 (m, 2H), 7.15–7.32 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 0.63, 4.74, 14.07, 31.76, 36.93, 55.52, 73.22, 80.50, 81.71, 125.64, 128.27, 128.45, 142.39; *m/z* (CI–MS) 232 ([M + NH_4]$^+$, 9%), 192 (27%), 176 (100%), 159 (50%); HRMS (CI +) predicted for $C_{15}H_{22}NO$ 232.1715, found 232.1714.

Tributyl-[3-(1-cyclopropyl-3-phenylpropoxy)-propenyl]-stannane (**10**): To a dried and degassed solution of the propargyl ether **9** (200 mg, 0.93 mmol) in benzene (20 cm^3) was added tributyltin hydride (0.80 cm^3, 2.80 mmol) and AIBN (12 mg, 0.08 mmol). The solution was heated to reflux under an atmosphere of nitrogen for 4 h. The cooled residue was concentrated *in vacuo* and purified by flash chromatography (silica, 100% petrol then 5% Et_2O in petrol) to give the stannane **10** (33 mg, 46%) as a yellow oil; υ_{max} (thin film)/cm^{-1} 3078, 3002, 2923, 2853, 1604; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.02–0.15 (m, 1H), 0.35–0.60 (m, 2H), 0.60–0.70 (m, 1H), 0.85–1.05 (m, 16H), 1.25–1.40 (m, 6H), 1.40–1.62 (m, 6H), 1.90, 2.10 (m, 2H), 2.60–2.90 (m, 3H), 3.90–4.45 (m, 2H), 5.05–5.40 (m, 2H), 7.15–7.35 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 1.04, 4.66, 9.38, 13.71, 14.83, 27.28, 28.95, 31.92, 37.00, 72.54, 82.27, 125.58, 128.25, 128.39, 130.19, 142.60, 145.56; *m/z* (EI–MS) 449 ([M–Bu]$^+$, 100%), 393 (17%), 331 (9%), 291 (55%); HRMS predicted for [M–Bu]$^+$ $C_{23}H_{37}O^{120}Sn$ 449.1866, found 449.1876.

[3-Cyclopropyl-3-(3-iodoallyoxy)-propyl]-benzene (**11**): To a stirred solution of stannane **10** (0.44 g, 0.87 mmol) in dichloromethane (20 cm^3) was added, portionwise, iodine (0.44 g, 1.74 mmol) at room temperature. The reaction mixture was stirred for 12 h in the dark and quenched with sodium thiosulfate (saturated aqueous solution) (20 cm^3). The aqueous layer was extracted with dichloromethane (3 × 20 cm^3). The combined organic layers were dried ($MgSO_4$), concentrated *in vacuo* and purified by flash chromatography (silica, 2% Et_2O in petrol) to give a mixture of *E* and *Z* iodoalkenes **11** (0.24 g, 81%) as a yellow oil; R_F = 0.50 (2% EtOAc in petrol); υ_{max} (thin film)/cm^{-1} 3077, 3001, 2921, 2853, 1603; ^{1}H NMR (300 MHz, $CDCl_3$) δ (–)0.03–(+)0.10 (m, 1H), 0.25–0.55 (m, 2H), 0.55–0.70 (m, 1H), 0.80–0.90 (m, 1H), 1.85–2.00 (m, 2H), 2.55–2.90 (m, 3H), 3.85–4.35 (m, 2H), 6.30–6.70 (m, 2H), 7.10–7.30 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 0.65, (4.30 + 4.35), 14.24, 31.38, 36.48, (70.00 + 70.96), (77.48 + 82.38), (81.78 + 82.62), (125.24 + 125.27), (127.89 + 127.95), 138.79, 141.84, 142.78; *m/z* (CI–MS) 360 ([M + NH_4]$^+$, 12%), 343 ([M + H]$^+$, 1%), 176 (100%); HRMS predicted for $C_{15}H_{23}INO$ 360.0824, found 360.0819.

1-Phenyl-hexan-3-one (**12**): To a dried and degassed solution of the alkenyl iodide **11** (0.02 M) (222 mg, 0.65 mmol) in benzene (32.5 cm^3) was added AIBN (6 mg, 0.04 mmol). The solution was heated at reflux under an atmosphere of nitrogen whereupon a solution of tributyltin hydride (0.23 cm^3, 0.85 mmol, 1.3 equiv) and AIBN (6 mg, 0.04 mmol, 0.1 equiv) in benzene (5 cm^3) was added *via* a syringe pump over 20 h. After addition was complete, the solution was maintained at reflux for a further 16 h. The solution was cooled, added to KF (saturated aqueous solution) (30 cm^3) and stirred for 24 h. To the biphasic solution was added water (30 cm^3) and the aqueous layer was separated and extracted with EtOAc (3 × 30 cm^3). The combined organic layers were washed with water (3 × 20 cm^3), NaCl (saturated aqueous solution) (2 × 20 cm^3) and water (20 cm^3). The organic layer was dried ($MgSO_4$), concentrated *in vacuo* and purified by flash chromatography (silica, 100% petrol then 0.5% Et_2O in petrol) to give the ketone **12** (38 mg, 33%) as a yellow oil; R_F = 0.29 (10% Et_2O in petrol); υ_{max} (thin film)/cm^{-1} 2961, 2872, 1712, 1604; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.89 (t, *J* = 7.4, 3H), 1.59 (sx, *J* = 7.4, 2H), 2.39 (t, *J* = 7.4, 2H), 2.72 (t, *J* = 7.5, 2H), 2.90 (t, *J* = 7.5, 2H), 7.10–7.30 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.70, 17.20, 29.72, 44.17, 44.91, 125.94, 128.29, 128.44, 141.14, 210.28; MS *m/z* (EI–MS) 176 (M^+, 83%), 133 (53%), 105 (95%), 91 (100%); HRMS predicted for $C_{12}H_{16}O$ 176.1201, found 176.1200.

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