in an autoclave for 48 hours at 100℃ and 20.4 atmospheres. After cooling to room temperature, the autoclave was opened and the yellow homogeneous solution was passed through Celite, and the filtrate was concentrated by rotary evaporation. The carboxylic esters were purified by silica gel thin-layer chromatography using 2 : 1 hexane/ethyl acetate as the developer. The ratio of esters was determined by ^{1}H-NMR and by GC analyses, and by comparison with authentic materials in most cases.

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Hydroacylation of Alkynes with Alkylpentacarbonylchromate Anions

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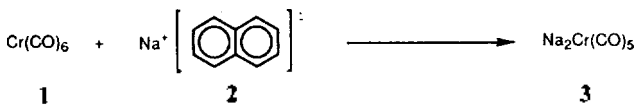
Various alkynes were hydroacylated with alkylpentacarbonylchromates in the presence of triphenylphosphine to give α,β-unsaturated ketones in good yields. The alkylpentacarbonylchromates were generated *in situ* from alkyl halides and disodium pentacarbonylchromate, $Na_2Cr(CO)_5$.

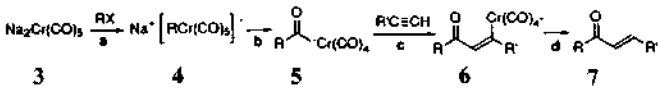
Introduction

In the last two decades, well defined direct carbonylations of organic compounds were developed to synthesize various carbonyl compounds. Some of these attempts involved fixation of carbon monoxide to non-carbonyl containing precursor using transition metal complexes. In this carbonylation chemistry external carbon monoxide which had to be introduced in high pressure[1] and special active catalysts[2] were needed. Others were focused on the reaction of transition metal complexes with acyl moiety were designed to introduce the carbonyl group[3]. These types of reactions needed to handle toxic carbon monoxide gas and involve special catalysts. Therefore they were not used widely for preparative methods of carbonyl compounds.

The preparation of a highly reactive species, disodium pentacarbonylchromate **3**, was reported by Ellis.[4] And a modified procedure was developed by Hegedus by the reaction of chromium hexacarbonyl **1** with sodium naphthalenide **2**.[5]



1 **2** **3**

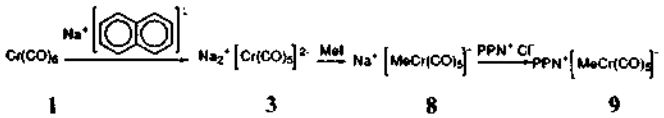


3 **4** **5** **6** **7**

Scheme 1.

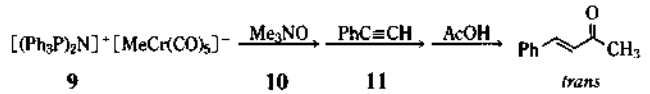
Treatment of this highly reactive species **3** with alkyl halides gives alkylpentacarbonylchromate monoanion complex **4** *via* nucleophilic oxidative addition.[6] However, due to its coordinatve saturation, these complexes **4** are fairly unreactive. Thus, it occurred to us that, if possible, intramolecular migratory insertion of an alkyl group to the carbonyl group on chromium metal in **4** would produce acyltetracarbonylchromate anion **5**, which is available for further reaction as shown in Scheme 1.

Consequently, the reaction of various alkylpentacarbonylchromate anions with alkynes was examined to synthesize directly α,β-unsaturated ketones. Easy preparation of these complexes may render us an advantage for this reaction. Various acyl groups are generated from migratory insertion, to carbon monoxide, of alkyl ligands on chromium metal, which are to be originated from alkyl halides.



Scheme 2.

Table 1. Hydroacylation of phenylacetylene with PPN Salt **9**



Entry	9	10		11		Yield[a]
	equiv	equiv	Rxn Temp	equiv	Rxn Temp	
1	1.0	–		1.0	rt	17%
2	1.0	1.0	0℃	1.0	rt	41%
3	1.0	1.0	0℃	1.0	rt[b]	39%
4	1.0	1.0	rt	1.0	rt	38%
5	1.5	–		1.0	rt[c]	34%
6	2.0	3.1	−78℃	1.0	−78℃ -0℃	48%
7	2.0	4.0	0℃	1.0	rt	48%

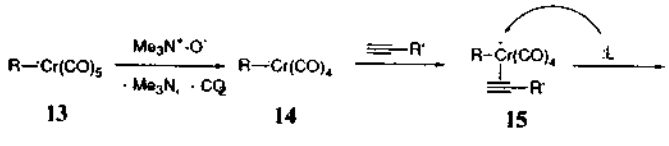
[a]Isolated yields based on phenylacetylene. [b]Work-up with dilute HCl (0.1 N 25 m*l*) and dilute AcOH (0.1 N 25 m*l*) was used in other cases. [c]Under 100,000 psi.

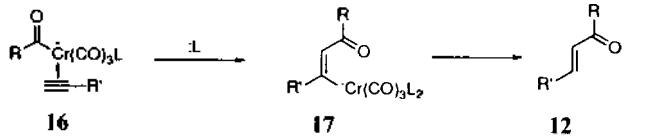
Results and Discussion

First, in order to find out the optimum condition of hydroacylation of alkynes with alkylpentacarbonylchromate, bis (triphenylphosphoranylidene)ammonium (PPN) salt of alkylpentacarbonylchromate anion was prepared in THF solution: The reaction of chromium hexacarbonyl **1** with sodium naphthalenide **2** at −78℃ gave a dark suspension, which was warmed up to ambient temperature to give a dark orange clean solution of disodium pentacarbonylchromate **3**.[5] Subsequent methylation with excess methyl iodide at room temperature provided sodium methylpentacarbonylchromate **8**. The corresponding PPN salt **9** was obtained in moderate yield by the addition of bis(triphenylphosphoranylidene)ammonium chloride (PPN^+Cl^-) to the resulting yellow solution (Scheme 2).

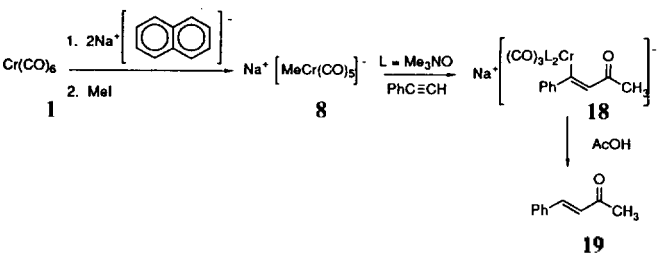
Our initial study was focused on the feasibility of conversion of the methylpetacarbonylchromate anion **9** to an acyl metal species, which might behave as a source of acyl moiety upon interaction with unsaturated organic compounds such as alkynes. Reaction of phenylacetylene **11** as a model substrate with the PPN salt **9** with varing stoichiometries in the presence of some additives was studied under various conditions. Thus, this reaction even without any additive did provide *trans*-4-phenyl-3-buten-2-one **12**, albeit in 17% yield. *cis*-Isomer could not be detected in all cases. Addition of trimethylamine N-oxide **10** improved the yield slightly but not much to a synthetically useful level. The results are shown in Table 1.

The idea of addition of trimethylamine N-oxide **10** was to make it more facile in the coordination of phenylacetylene to the vacant coordination site created by expulsion as CO_2 of one of the carbonyl group of metal carbonyl.[7] (Scheme 3)





Scheme 3.



Scheme 4.

Table 2. Hydroacylation of Phenylacetylene with *in situ* generated Sodium Methylpentacarbonylchromate

Entry	$Cr(CO)_6$[a] (equiv)	PhC≡CH (equiv)	Rxn Temp.	Additive (equiv)	Yield[c]
1	2	1		Me_3NO (2)	32%
2	4	1	−78℃ -rt	Me_3NO (1)	21%
3	4	1		Me_3NO (4)	56%
4	4	1	rt	NMMO[b] (4)	74%

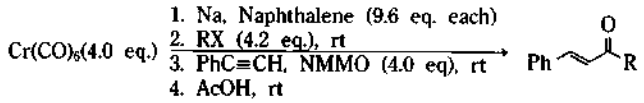
[a]Naphthalenide was added to the solution of $Cr(CO)_6$ at −78℃. [b]NMMO: N-Methylmorpholine N-oxide. [c]Isolated Yields based on phenylacetylene.

Unfortunately, various equivalents of trimethylamine N-oxide did not provide much difference and gave again low yields as shown in Entries 2, 6, and 7 of Table 1.

Thus another approach was investigated to develope a new hydroacylation procedure, where the *in situ* generated methylpentacarbonylchromate complex was used to prevent the effect of bulky PPN cation (Scheme 4). A practical advantage of this approach appears to be the avoidance of isolation of metallic species such as **3**, which was moisture and oxygen sensitive. Various conditions of the hydroacylation of phenylacetylene with *in situ* generated methylpentacarbonylchromate **3** were examined, and the proper condition of this reaction was obtained (Entry **4**). And N-methylmorpholine N-oxide, instead of trimethylamine N-oxide, gave higher yields. These results of optimization are summarized in Table 2.

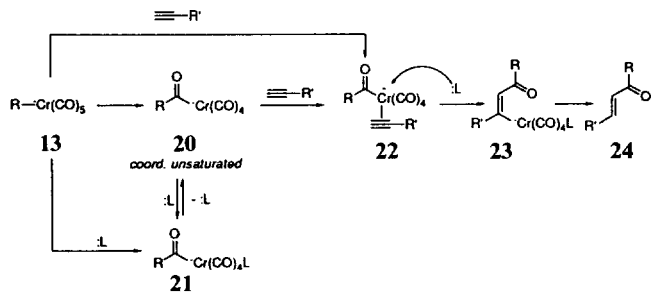
Having succeeded in dveloping a proper condition with methyl iodide, reactions of the dianion with other alkyl halides and subsequent reactions with phenylacetylene were carried out. Good yields were obtained in the reaction of primary alkyl halide, but the reaction of secondary alkyl halide gave poor yield (Entry 7 in Table 3) as expected, presumably due to the low reactivity of the secondary alkyl halide for

Table 3. Hydroacylation of Phenylacetylene with Various *in situ* Generated Alkylpentacarbonylchromate Complexes in the Presence of NMMO



Entry	RX	Product	Yield[a]
1	MeI	*trans*-MeCOCH=CHPh	74%
2	MeI	*trans*-MeCOCH=CHPh	56%[b]
3	MeI	*trans*-MeCOCH=CHPh	68%[c]
4	*n*-PrBr	*trans*-*n*-PrCOCH=CHPh	51%
5	*n*-BuI	*trans*-*n*-BuCOCH=CHPh	75%
6	*n*-OctBr	*trans*-*n*-OctCOCH=CHPh	44%
7	*i*-BuCl	*trans*-*i*-BuCOCH=CHPh	7%

[a]Isolated yields based on phenylacetylene. [b]Me_3N-O was used instead of NMMO. [c]*t*-BuOO$^-$Li$^+$ was used in place of NMMO.



Scheme 5.

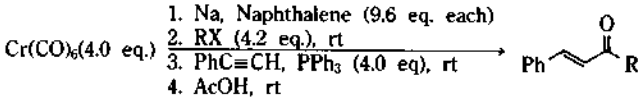
the nucleophilic oxidative addition and high tendency to E2 reaction (step a in Scheme 1). The results are shown in Table 3.

As mentioned earlier, even in the presence of trimethylamine N-oxide, treatment of phenylacetylene with the PPN salt **4** gave the product in low yield. A way of looking at it is that migratory insertion of an alkyl group to a carbon monoxide on chromium preceeds coordination of phenylacetylene. With that assumption in hand, the overall reaction may proceed along the path shown in Scheme 5. Also, it is to be noted that extra ligands may be necessary in two migratory insertion steps, namely migratory insertion of an alkyl group to coordinated carbon monoxide and that of an acyl group to coordinated alkyne.

In this regard, it was shown that square pyramidal acylmanganese complex **25** are configurationally stable for low spin complex and have unoccupied site for ligand.[8] The acyltetracarbonylchromate anion complexes **26**, which were generated by the migratory insertion of metal carbonyl to alkyl ligands in the complexes of alkylpentacarbonylchromate complexes, were isoelectronic with **25** and thus presumed to have the same structure.

Thus, subsequent efforts were focused on finding a suitable entering ligand which is able to accelerate the migratory insertion steps. As shown in the Scheme 5, the vacant site which was generated by the migration of acyl moiety had to be occupied by incoming ligand. It was assumed that triphenylphosphine might be able to play this role. Gratifyingly, the desired products were obtained in good yield (Table 4).

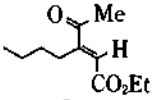
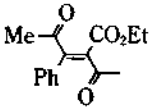
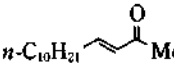
Table 4. Effect of PPh_3 in Hydroacylation of Phenylacetylene with Various Alkylpentacarbonylchromate Complexes



Entry	RX	Product	Yield[a]
1	MeI	*trans*-MeCOCH=CHPh	89%
2	*n*-PrBr	*trans*-*n*-PrCOCH=CHPh	72%
3	*n*-BuI	*trans*-*n*-BuCOCH=CHPh	88%
4	*n*-OctI	*trans*-*n*-OctCOCH=CHPh	71%
5	*i*-BuCl	*trans*-*i*-BuCOCH=CHPh	46%

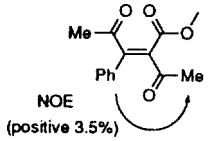
[a]Isolated yields based on phenylacetylene.

Table 5. Hydroacylation of Functionalized Alkynes with *in situ* Prepared Sodium Methylpentacarbonylchromate

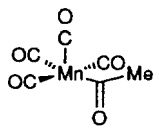
Entry	Alkyne	Products		Yield[a]
1	*n*-$C_4H_9C{\equiv}CCO_2Et$		(27)[f]	32%[b]
2	*n*-$C_4H_9C{\equiv}CCO_2Et$			10%[c]
3	$PhC{\equiv}CCO_2Et$		(28)[f]	52%[b]
4	$PhC{\equiv}CCO_2Et$			35%[c]
5	1-Dodecyne			47%[b]
6	1-Dodecyne			33%[c]
7	1-Dodecyne		(29)	22%[d]

[a]Isolated yields based on alkynes. [b]PPh_3 was used as an additive. [c]NMMO was used as an additive. [d]*t*-BuOO$^-$Li$^+$ was used as an additive. [f]In the NOE differential spectrum positive effect was observed between vinyl proton and protons of acetyl group. [f]The spectral data of this compound, **28**, are given below.

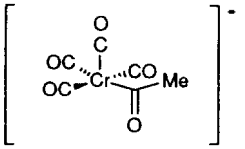
IR: 1815 (s), 1710 (s), 1662 (s) cm^{-1}. ^{1}H-NMR: δ 7.3 (m, 5H), 4.13 (q, 2H), 2.52 (s, 3H), 1.90 (s, 3H), 1.12 (t, 3H). ^{13}C-NMR: δ 178.15 (C=O), 167.13 (C=O), 162.91 (C=O), 138.56 (Ph), 128.71 (Ph), 127.88 (Ph), 126.29 (Ph), 115.89 (?), 60.11 (OCH_2), 51.98 (?), 21.69 (Me), 13.74 (Me), 13.67 (OCH_2CH_3). GC-MS (relative intensity) 260 (M, 31), 217 (M-COMe, 77), 189 (M-COMe-CO, 45), 159 (M-CO-CO_2Et, 90), 43 ($COCH_3$, 100).



To show the applicability of this reaction to a wide variety of alkynes, several alkynes having other functional groups



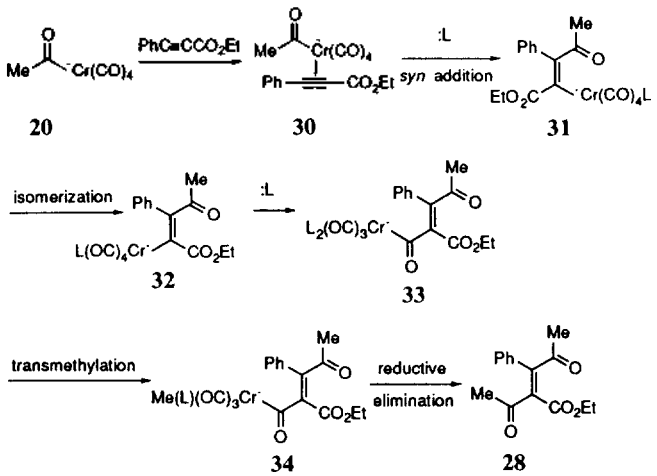
25



26

were investigated but only moderate yields were obtained (Table 5).

In these cases especially with conjugated alkyne, instead of hydroacylation, some double acylation has occurred. Thus, when ethyl phenylpropiolate was sujected to the same reaction condition, a double acylated product **28** was obtained. The formation of this compound can be rationalized as following.



This reaction was surprising in two aspects: The second migratory insertion reaction of acyl group to coordinated alkyne in the usual *syn* manner was followed by Z to E isomerization, which was not observed with simple alkynes. Secondly, it is not clear at this moment the source of methyl group in the second acetyl group. One thing that is clear is that the methyl group was not originated from excess methyl iodide. In one of experiments, after methylation of disodium pentacarbonylchromate with methyl iodide, all the solvents were evaporated off to get rid of excess methyl iodide which might be present. Addition of fresh solvent (THF) and subsequent reaction with ethyl phenylpropiolate under otherwise same condition again provided the doubly acetylated product **28**. Clearly, some more fundamental insight on this reaction is needed.

Experimental

General. Small- and medium-scale purifications (20 mg-2 g) were performed by radial chromatography by using Harrison Research Chromatotrons on plates of 1-, 2-, or 4-mm thickness made with Merck silica 60 PF_{254} containing gypsum. Flash chromatography was performed on a Tokyo Rikagikai EF-10 with Merck 230-400 mesh silica gel. ^{1}H-NMR was obtained on a Varian EM-360A (60 MHz) or a Varian Gemini 300 (300 MHz) spectrometer. NMR Spectra were recorded in ppm (δ) relative to Me_4Si (δ 0.00) as an internal standard unless stated otherwise and are reported as follows: chemical shift, multiplicity (br=broad, s=singlet, d=doublet, t=triplet, q=quartet), coupling constant and integration. Infrared spectra were obtained on a Shimazu IR-400 or Mattson Galaxy 2000 spectrometers. All reactions involving organometallic reagents were carried out under an inert atmosphere of nitrogen or argon. Solvents and liquid reagents were transferred using hypodermic syringes or double ended needle. Tetrahydrofuran and diethyl ether were distilled from sodium benzophenone ketyl under a nitrogen atmosphere just prior to use. Chromium hexacarbonyl (Strem chemicals inc.), naphthalene (Baker), sodium lump (Fluka), phenylacetylene (Aldrich), methyl iodide (Aldrich), and other alkyl halides (Aldrich) were obtained from commercial suppliers and used without further purifications. The following chemicals were prepared according to the literature procedure.[9]: 1-dodecyne, ethyl phenylpropiolate, ethyl 2-heptynoate.

Preparation of Disodium Pentacarbonylchromate Dianion (3). To sodium (0.45 g, 19.6 mmol) in THF (38 m*l*) placed in a thoroughly dried 50 mL round bottomed flask, naphthalene (2.46 g, 19.2 mmol) was added under nitrogen. Dark green color appeared instantaneously as naphthalene dissolved, and the solution of mixture was stirred for 2 h. The THF solution of naphthalenide was transferred under nitrogen to the suspension of chromium hexacarbonyl (1.76 g, 8 mmol) in THF (10 m*l*) in another 100 m*l* round bottomed flask over 1 h at −78℃ and the newly formed dark suspension of mixture was allowed to warm up to room temperature and stirred for 4 h to give a clear and dark brown solution which was ready for further synthesis. IR (in THF) 1817(s), 1769(s) cm^{-1}.

Preparation of PPN Salt of Methylpentacarbonylchromate Complex (4). To dark yellow solution of 5 mmol of (3), was added excess methyl iodide through a hypodermic syringe and the solution of mixture was stirred for 1 h. A solution of PPN Cl (2.99 g, 5.2 mmol) dissolved in MC (25 m*l*) was transferred to the resulting solution at room temperature and stirred overnight. Solvent was evaporated to give dark yellow solid. Recrystallization of this solid gave 2.54 g (68%) of desired product (4). IR (KBr) 2017, 1923, 1884, 1840 cm^{-1}. NMR (Aceton-d_6/MC) δ 8.5 (s, 30H), −2.0 (s, 3H).

Reaction of (4) with Phenylacetylene. To the PPN salt (4) (2.98 g, 4 mmol), dissolved in 20 m*l* of THF in a 50 m*l* round bottomed flask equipped with a magnetic stirring bar, a septum inlet and a nitrogen-filled balloon, was added 0.22 m*l* of phenylacetylene (2 mmol) dropwise at room temperature and the resulting solution was stirred for 1 h, and 25 m*l* of 0.1 N AcOH was added to the resulting dark red solution. The aqueous layer was extracted with ether. The resulting organic layer was dried over $MgSO_4$. Solvents were removed under a reduced pressure, and the purification of the residue by Chromatotron chromatography gave 0.14 g (0.96 mmol, 48%) of *trans*-4-phenyl-3-buten-2-one. TLC (20% Ethyl acetate/*n*-hexane) R_f 0.42 IR (neat) 1668, 1608 cm^{-1}. NMR ($CDCl_3$) δ 7.42 (d, J=16.0 Hz, 1H), 7.40 (m, 5H), 6.65 (d, 1H, J=16.3 Hz), 2.30 (s, 3H). GC-MS 146 (M, 45), 131 (M-Me, 82), 103 (PhCHCH, 100), 77 (C_6H_5, 57), 43 ($COCH_3$, 25).

Reaction of Phenylacetylene with (3) and Alkyl Halides, A General Procedure. To a solution of disodium pentacarbonylchromate dianion (8 mmol) an alkyl halide (8.2 mmol) were added through a septum *via* a syringe at ambient temperature and the solution of mixture was stirred for 1 h. To this was added phenylacetylene (2 mmol) by a syringe at ambient temperature. After 1-2 h, a THF solution of NMMO (method A) or PPh_3 (method B) was added

through septum by a double ended needle. The resulting solution was stirred for 1 h and then poured into 50 ml of AcOH (0.1 N). The aqueous layer was extracted with ether and dried with $MgSO_4$. The solvents were removed under a reduced pressure, and the residue was purified by flash chromatography with elution first with hexane to remove naphthalene. Further elution with 10% ethyl acetate/*n*-hexane gave the desired *trans*-enones. *trans*- and *cis*-isomers were determined by the analysis of GC and ^{1}H-NMR. Physical data are given below.

4-Phenyl-3-buten-2-one. 74% (method A) and 89% (method B). TLC (20% Ethyl acetate/*n*-hexane) R_f 0.42. IR (neat) 1668, 1608 cm^{-1}. NMR ($CDCl_3$) δ 7.42 (d, J=16.0 Hz, 1H), 7.40 (m, 5H), 6.65 (d, J=16.3 Hz, 1H), 2.30 (s, 3H). GC-MS 146 (M^+), 131, 103, 77, 43.

1-Phenyl-1-hexen-3-one. 51% (method A) and 72% (method B). TLC (10% Ethyl acetate/*n*-hexane) R_f 0.48. IR (neat) 1666, 1612 cm^{-1}. NMR ($CDCl_3$) δ 7.52 (d, J=16.2 Hz, 1H), 7.5 (m, 2H), 7.35 (m, 3H), 6.70 (d, J=16.5 Hz, 1H), 2.57 (t, J=7.4 Hz, 2H), 1.65 (m, J=7.4 Hz, 2H), 0.9 (t, J=7.5 Hz, 3H). GC-MS 174 (M^+), 131, 103, 77, 41.

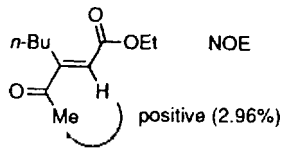
1-Phenyl-1-hepten-3-one. 75% (method A) and 88% (method B). TLC (20% Ethyl acetate/*n*-hexane) R_f 0.66. IR (neat) 1689, 1612 cm^{-1}. NMR ($CDCl_3$) δ 7.56 (d, J=16.2 Hz, 1H), 7.55 (m, 2H), 7.35 (m, 3H), 6.75 (d, J=16.3, 1H), 2.65 (t, J=7.4 Hz, 2H), 1.65 (m, J=7.3 Hz, 2H), 1.35 (m, J=7.5 Hz, 2H), 0.92 (t, J=7.3 Hz, 3H). GC-MS 188 (M^+), 146, 131, 103, 77.

1-Phenyl-1-undecen-3-one. 44% (method A) and 71% (method B). TLC (20% Ethyl acetate/*n*-hexane) R_f 0.62. IR (neat) 1656, 1601 cm^{-1}. NMR ($CDCl_3$) δ 7.58 (d, J=16.4 Hz, 1H), 7.55 (m, 2H), 7.40 (m, 3H), 6.74 (d, 1H, J=16.3 Hz), 2.65 (t, 2H, J=7.6 Hz), 1.67 (m, 2H), 1.28 (m, 10H), 0.89 (t, 3H, J=6.4 Hz). GC-MS 244 (M^+), 146, 131, 103, 77, 43, 41.

5-Methyl-1-phenyl-1-hexene-3-one. 7% (method A) and 46% (method B). TLC (10% Ethyl acetate/*n*-hexane) R_f 0.42. IR (neat) 1724, 1670 cm^{-1}. NMR ($CDCl_3$) δ 7.56 (d, J=16.4 Hz, 1H), 7.55 (m, 2H), 7.40 (m, 3H), 6.75 (d, J=16.1 Hz, 1H), 2.52 (d, J=7.0 Hz, 2H), 2.25 (m, J=6.8 Hz, 1H), 0.98 (d, J=6.6 Hz, 6H). GC-MS 188 (M^+), 146, 131, 103, 77.

3-Tetradecen-2-one. 33% (method A), 47% (method B) and 22% yield (*t*-BuOO$^-$Li$^+$ as additive). TLC (10% Ethyl acetate/*n*-hexane) R_f 0.45. IR (neat) 1678, 1628 cm^{-1}. NMR ($CDCl_3$) δ 6.81 (m, J=16 Hz, J=6.9, 1H), 6.09 (m, J=15.9 Hz, J=1.6 Hz, 1H), 2.24 (s, 3H), 1.44 (m, 3H), 1.27 (m, 16H), 0.88 (t, J=6.5 Hz, 3H), GC-MS 210 (M^+), 97, 71, 55, 43.

Ethyl *E*-2-acetyl-2-heptenoate. 10% (method A), and 32% (method B), TLC (10% Ethyl acetate/*n*-hexane) R_f 0.34. IR (neat) 1726, 1687, 1612 cm^{-1}. NMR ($CDCl_3$) δ 6.52 (s, 1H), 4.21 (q, J=6.9 Hz, 2H), 2.75 (m, J=6.9 Hz, 2H), 2.37 (s, 3H), 1.35 (m, 7H), 0.81 (t, J=6.0 Hz, 3H). GC-MS 198 (M^+), 152, 110, 109, 81, 43.



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