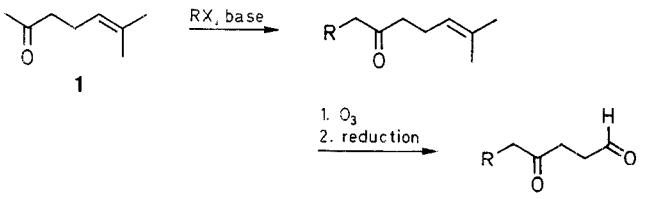
Synthesis of 2-Alkyl-2-cyclopenten-1-ones. A Versatile Kinetic Alkylation–Ozonolysis Procedure for the Preparation of γ-Ketoaldehydes

Niall W.A. Geraghty,* Noreen M. Morris

Chemistry Department, University College, Galway, Ireland

A range of 2-alkyl-2-cyclopenten-1-ones including the prostaglandin precursor 2-(6-methoxycarbonylhexyl)-2-cyclopenten-1-one and the jasmonoid precursor 2-[(*Z*)-2-pentenyl]-2-cyclopenten-1-one, have been prepared by a short synthetic route which begins with 6-methyl-5-hepten-2-one and generates the key 1,4-ketoaldehyde intermediates by a kinetic alkylation–ozonolysis procedure.

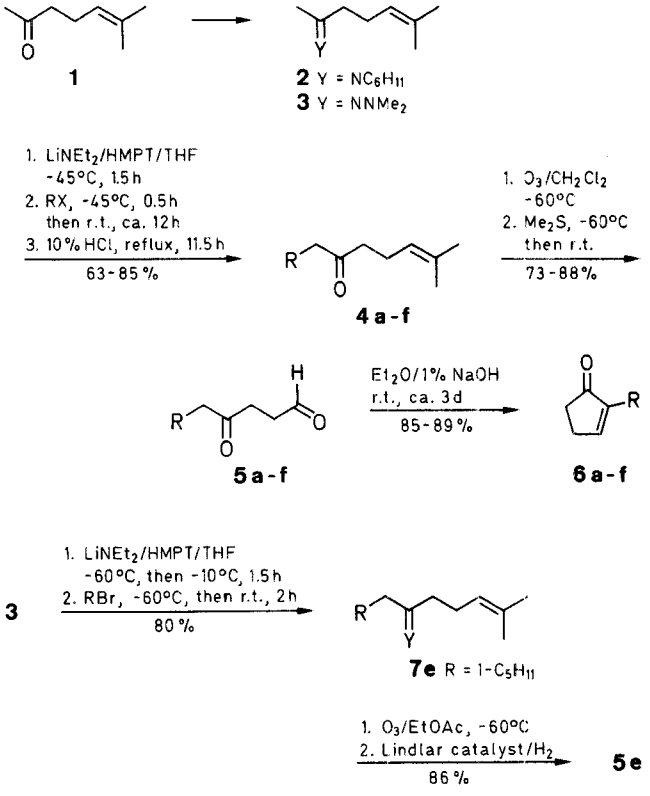
Despite the large number of methods available in the literature,[1,2] there is a continuing effort to devise new ways of synthesizing 2-alkyl-2-cyclopenten-1-ones. This effort is fueled by the importance of the materials themselves, and also by the limitations of the published procedures which can include both a lack of general applicability and also difficulties, such as a need for chromatography, in carrying out the procedure on a large scale. The approach described here uses a kinetic alkylation–ozonolysis procedure (Scheme **A**) to synthesize γ-ketoaldehydes[3] which are the most commonly used precursors of 2-alkyl-2-cyclopenten-1-ones.



Scheme A

The starting material used is the cheap, readily available, 6-methyl-5-hepten-2-one (**1**) which is kinetically alkylated in the 1-position as its cyclohexylimine **2** or *N,N*-dimethylhydrazone **3** (Scheme **B**). Regiospecific alkylation is achieved in this case using lithium diethylamide in the presence of hexamethylphosphoric triamide (HMPT).[4] However, as the same specificity has been achieved for this and related ketones, in both acylation and alkylation reactions and using a variety of other bases,[5–8] it is clear that the choice of base is not critical. Acid hydrolysis of the alkylated imine gives the corresponding unsaturated ketone **4**, whose purity after distillation is, in most cases, approximately 95% (GLC, Table 1); the only impurity is the starting material **1**. **4** is converted to the γ-ketoaldehyde **5** using ozone followed by dimethyl sulfide. This process results in the loss of the levulinaldehyde which is presumably formed from **1** on ozonolysis, and allows the γ-ketoaldehydes **5** to be isolated in a pure form by distillation. In the case of the hydrazone **7** the keto group may be

regenerated and the alkene cleaved in a single step using ozone and either dimethyl sulfide or hydrogen and Lindlar catalyst. The overall yield of γ-ketoaldehyde is approximately the same for both the imine and the hydrazone routes but the latter does avoid the need for dilute aqueous acid and has thus advantages for the synthesis of molecules with acid labile groups. Although in principle the conversion of the γ-ketoaldehyde **5** to the cyclopentenone **6** is a well established procedure there is by no means agreement in the literature[10] as to precise combination of base and solvent which should be used to obtain the optimum yield. An evaluation of a number of solvent/base combinations led to the conclusion that the two-phase ether/aqueous sodium hydroxide system suggested by Stork[11] is, despite the long reaction time, the method of choice for the cyclization of all but one (**5g**, see below) of the γ-ketoaldehydes studied as it gives a high yield of an easily purified product.

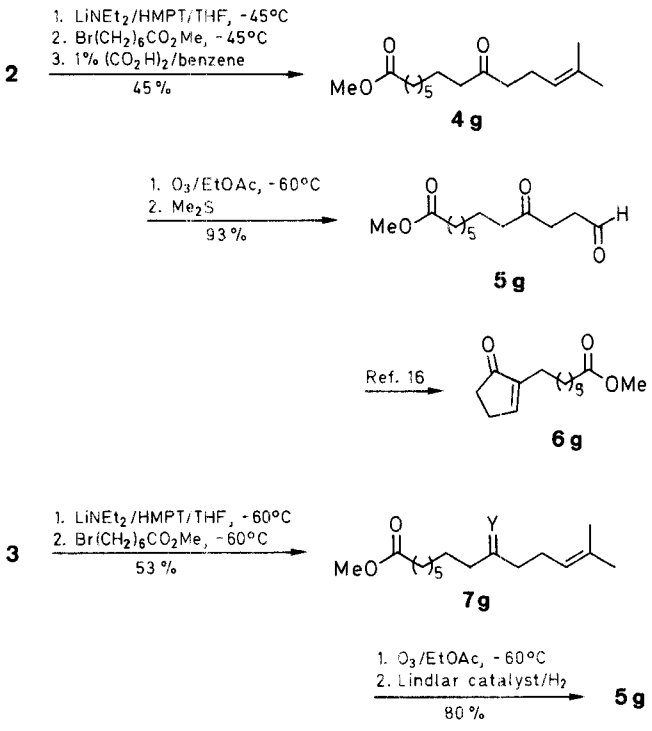


4–7	R	4–7	R
a	CH_3	d	$(CH_2)_3CH_3$
b	CH_2CH_3	e	$(CH_2)_4CH_3$
c	$(CH_2)_2CH_3$	f	$(CH_2)_5CH_3$

Scheme **B**

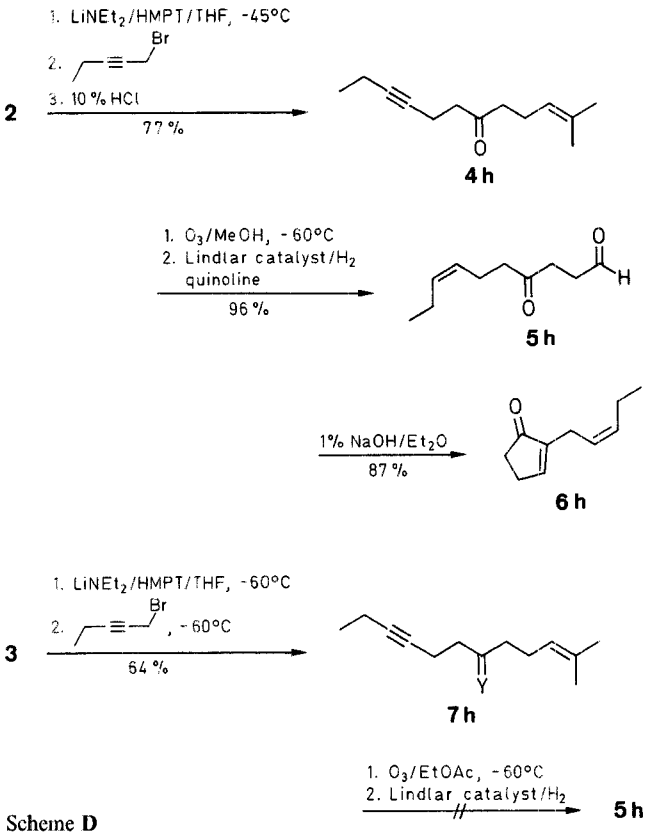
The procedure outlined above was initially used to prepare a series of 2-alkyl-2-cyclopenten-1-ones with saturated side chains (Table 2, **6a–f**). It was subsequently applied to the synthesis of two important 2-alkyl-2-cyclopenten-1-ones with functionalized side chains.

2-(6-Methoxycarbonylhexyl)-2-cyclopenten-1-one **(6g)** has been used as an intermediate in the synthesis of certain prostaglandins and a number of methods[12-14] for its preparation has appeared in the literature. The approach described here can be used (Scheme **C**) to prepare its precursor **5g** in very few steps and without the need for chromatography. If the hydrazone **3** is used the yield for the alkylation step is higher than with the imine **2** and the possibility of regenerating the ketone concurrently with the cleavage of the alkene removes the need to use aqueous acid to achieve this transformation. Methods[15] for the selective hydrolysis of the imine group in an iminoester also require very large quantities of solvent and thus lead to problems if the reaction is to be scaled up. The yield in the alkylation step is moderate but as the effect of changing the base system used was not investigated it is possible that the use of a different base would result in an enhanced yield. The cyclization of **5g** using aqueous sodium hydroxide/ether gave **6g** in reasonable yield (72%) but not in an acceptably pure form (78% by GLC) and thus the two-phase system is inferior in this case to the use of sodium methoxide in methanol which has become the standard method of converting **5g** to **6g**.[12,14,16]



Scheme **C**

2-[(*Z*)-2-Pentenyl]-2-cyclopenten-1-one **(6h)** has been frequently used[1,17] as an intermediate in the synthesis of methyl (±)-jasmonate; it can be prepared using the alkylation–ozonolysis procedure (Scheme **D**) with an alkyne being used as a protected *Z*-alkene, into which it is converted during the reduction of the ozonide obtained from **4h**, by the simple expedient of using Lindlar catalyst and hydrogen in place of the dimethyl sulfide previously used. The amount of ozone added must be carefully controlled as alkynes are more susceptible to attack by ozone[18] than the early literature would suggest. The γ-ketoaldehyde **5h** can thus be prepared from the imine **2**; the preparation of **6h** is completed by the base catalyzed two-phase cyclization of **5h**. The alkylation step is also quite efficient if the hydrazone **3** is used but when an attempt is made to convert the product **7h** to **5h** using ozone followed by Lindlar catalyst and hydrogen, a complex mixture of products is obtained from which no γ-ketoaldehyde could be



Scheme D

isolated; a mixture of products is also obtained if dimethyl sulfide is used as reducing agent. It would appear then that a hydrazone cannot be selectively ozonized in the presence of a carbon–carbon triple bond.

Thus the kinetic alkylation–ozonolysis procedure described here allows a wide range of γ-ketoaldehydes to be prepared including the key intermediates **5g** and **5h** which have been the goal of much synthetic work in this area. The principal advantages of the procedure are the inexpensive nature of the starting materials, the potential for carrying through the procedure on a large scale, and the ease of purification of the products.

Table 2. Preparation of 2-Alkyl-2-cyclopenten-1-ones **6** using the Two-Phase System[11] Et_2O/NaOH

Product	Yield (%)[a]	bp (°C)/Torr	Lit. bp (°C)/Torr
6a	85 (88)	48–50/0.1	59/16[24]
6b	89	65–70/1	69–72/16[25]
6c	88 (91)	68–72/1	59–60/1.3[26]
6d	89	70–74/1	98–100/12[25]
6e	89	72–76/1	60/0.2[27]
6f	89	76–78/1	88–89/1[25]
6h	87 (91)	64–66/0.05	76/0.1[23]

[a] Yield of product purified by distillation. The purity was in general ≥95% GLC (Carbowax 20M) and in those cases where it was less (value in parentheses) an analytically pure sample was obtained on chromatography or further distillation.

Table 1. Preparation of Unsaturated Ketones **4** and γ-Ketoaldehydes **5**

Product	Starting Material	Ketone **4**			Hydrazone **7**			γ-Ketoaldehyde **5**		
		Yield[a,b,c] (%)	bp (°C)/Torr	Molecular Formula or Lit. bp (°C)/Torr	Yield[a,b,c] (%)	bp (°C)/Torr	Molecular Formula	Yield[a,b,c] (%)	bp (°C)/Torr	Lit. bp (°C)/Torr
a	**2**	63 (86)	53–58/1	77–84/15[19]	–	–	–	73	46–48/1	70/16[21]
b	**2**	72 (93)	60–65/1	104–108/27[20]	–	–	–	79	50–52/1	86–87/40[22]
c	**2**	82 (93)	68–74/1	$C_{11}H_{20}O$ (168.3)	–	–	–	77	70–75/3	78–80/20[22]
d	**2**	83	78–84/1	$C_{12}H_{22}O$ (182.3)	–	–	–	80	76–80/3	92–94/15[22]
e	**2**	85	85–89/1	$C_{13}H_{24}O$ (196.3)	–	–	–	86	78–80/0.1	79–80/2[22]
e	**3**	–	–	–	80	96–98/1	$C_{15}H_{30}N_2$ (238.4)	86	78–80/0.1	79–80/2[22]
f	**2**	84	90–98/1	$C_{14}H_{26}O$ (210.4)	–	–	–	88	96–98/0.4	83–84/2[22]
g	**2**	45 (88)	116–120/0.4	$C_{16}H_{28}O_3$ (268.4)	–	–	–	93	140–142/0.1	–[23]
g	**3**	–	–	–	53	140–144/0.5	$C_{18}H_{34}N_2O_2$ (310.5)	80	140–142/0.1	–[23]
h	**2**	77	94–96/0.8	$C_{13}H_{20}O$ (192.3)	–		–	96 (89)	96–98/0.9	94/0.8[23]
h	**3**	–	–	–	64	96–98/2	$C_{15}H_{26}N_2$ (234.4)			

[a] Yield of product after distillation; the purity was in general ≥95% by GLC (Carbowax 20M, 150°C) and in those cases where it was less (value in parentheses), an analytically pure sample was obtained on chromatography or further distillation.

[b] The spectroscopic data for compounds **4a–f** and **5a–f** were unremarkable, those for **4d** and **5d** being representative: **4d:** IR (film): ν = 1711 cm^{-1}. ^{1}H-NMR ($CDCl_3$/TMS): δ = 0.97 (t, 3H, J = 7.3 Hz); 1.28 (m, 6H); 1.61 (s, 3H); 1.67 (s, 3H); 2.26 (m, 2H); 2.41 (m, 4H); 5.06 (br s, 1H). ^{13}C-NMR ($CDCl_3$/TMS): δ = 13.9, 17.6, 22.5, 22.55, 23.5, 25.6, 31.4, 42.7, 42.8, 122.9, 132.5, 211.1. **5d:** IR (film): ν = 1710 (CHO); 1705 cm^{-1} (CO). ^{1}H-NMR ($CDCl_3$/TMS): δ = 0.92 (m, 3H); 1.40 (m, 6H); 2.48 (t, 2H, J = 7.1 Hz); 2.73 (br s, 4H); 9.78 (br s, 1H). ^{13}C-NMR ($CDCl_3$/TMS): δ = 14.1, 28.9, 31.65, 34.7, 37.5, 42.8, 200.7, 209.1.

[c] Satisfactory microanalyses obtained: C ±0.32, H ±0.20, N ±0.12.

^{1}H- and ^{13}C-NMR were recorded at 270 and 68 MHz, respectively. The alkylating agents and other starting materials were dried and distilled before use. The solvents used were dried using standard procedures and were distilled.

6-Methyl-5-hepten-2-one Cyclohexylimine (2):
6-Methyl-5-hepten-2-one **1** (37.8 g, 0.3 mol), cyclohexylamine (29.7 g, 0.3 mol), and benzene (40 mL) are placed in a flask fitted with a Dean-Stark trap, and the mixture is refluxed until the theoretical amount of water (5.3 mL) is obtained (17 h). The solvent is removed under vacuum and the brown oil remaining is fractionally distilled using a Vigreaux column to give **2**; yield: 54.3 g (88%); bp 100–105°C/1 Torr.

$C_{14}H_{25}N$	calc.	C 81.09	H 12.15	N 6.75
(207.4)	found	80.99	11.80	6.71

IR (film): $\nu = 1658\ cm^{-1}$ (C=N).

^{1}H-NMR ($CDCl_3$/TMS): δ = 1.19–1.60 (m, 10H); 1.46 (s, 3H); 1.68 (s, 3H); 1.79 (s, 3H); 2.10 (br s, 4H); 3.22 (m, 1H); 5.10 (br s, 1H).

Compound **3** is prepared according to Ref. 6.

Alkylated Ketones 4a–f; General Procedure:[28]
$HNEt_2$ (12.15 g, 0.165 mol), HMPT (36 mL), benzene (33 mL), and finely cut Li (1.17 g, 0.165 mol) are stirred under nitrogen until all Li has dissolved (approximately 4.5 h). THF (45 mL) is added, and the red solution is cooled to −45°C; **2** (31.05 g, 0.15 mol) in THF (45 mL) is then added dropwise over 30 min, and the mixture is stirred at the same temperature for a further 1.5 h. The appropriate alkylating agent (0.18 mol) in THF (45 mL) is added (30 min) and the resulting straw coloured solution is left stirring at −45°C for 30 min and then at r.t. overnight. Following the addition of 10% HCl (250 mL) the stirred mixture is refluxed vigorously, the hydrolysis, which is monitored by IR, taking approximately 11.5 h. The mixture is extracted with Et_2O (3 × 50 mL), and the combined extracts are washed with 5% $NaHCO_3$ (2 × 60 mL). After drying over $MgSO_4$ the solvent is removed under vacuum giving the product **4** as a yellow oil which is purified by fractional distillation using a Vigreaux column.

4-Oxoalkanals 5a–f; General Procedure:
Ozone is passed through a gas dispersion tube into a stirred solution of the ketone **4** (0.05 mol) in CH_2Cl_2 (100 mL) at −60°C until the solution turns blue. The reaction vessel is then flushed with nitrogen and Me_2S (0.25 mol) is added. The stirred solution is allowed to warm to r.t., the progress of the reduction being monitored using starch-iodide paper. After removal of the solvent and excess Me_2S under vacuum, DMSO is removed by eluting the residue from a small amount of silica (15 g) with Et_2O (50 mL). [The DMSO may also be removed by the addition of water (10 mL) to the residue and subsequent continuous extraction with pentane (50 mL). This procedure results in a lower yield of 4-oxoalkanal **5**]. Removal of the solvent gives the product **5** as a brown oil which is purified by distillation through a Vigreaux column.

2-Alkyl-2-cyclopenten-1-ones 6a–f; General Procedure:[11]
The γ-ketoaldehyde (2.3 mmol) **5** is added to a mixture of Et_2O (15 mL) and 1% NaOH (10 mL). Stirring is continued until GLC analysis (Carbowax 20M, 150°C) indicates that conversion to the 2-alkyl-2-cyclopenten-1-one **6** is complete (approx. 3 d).

2-Methyl-2-dodecen-6-one *N,N*-Dimethylhydrazone (7e):
A solution of the hydrazone **3** (8.4 g, 0.05 mol) in THF (15 mL) is added dropwise over 30 min to a solution of $LiNEt_2$, prepared as before (0.39 g, 0.055 mol Li), at −60°C. The resulting solution is allowed to stand at −10°C for 1.5 h; the temperature is reduced to −60°C and 1-bromopentane (7.55 g, 0.05 mol) in THF (70 mL) is added dropwise. After 2 h at r.t. the mixture is diluted with Et_2O (150 mL), and the solution is washed with water (4 × 50 mL). After drying over K_2CO_3, removal of the solvent gives the product **7e** as a yellow oil which is purified by fractional distillation using a Vigreaux column; yield: 9.5 g (80%); bp 96–98°C/1 Torr.

$C_{15}H_{30}N_2$	calc.	C 75.52	H 12.67	N 11.79
(238.4)	found	75.49	12.81	11.72

IR (film): $\nu = 1628\ cm^{-1}$ (C=N).

^{1}H-NMR ($CDCl_3$/TMS): δ = 0.89 (t, 3H, J = 4.2 Hz); 1.30 (m, 6H); 1.48 (m, 2H); 1.61 (s, 3H); 1.67 (s, 3H); 2.26 (br s, 4H); 2.40 (s, 6H); 2.45 (m, 2H); 5.19 (br s, 1H).

^{13}C-NMR ($CDCl_3$/TMS): δ = 14.1, 22.7, 25.7, 25.95, 26.55, 27.3, 29.2, 29.65, 29.9, 31.7, 36.0, 36.3, 123.6, 131.9, 172.6.

Ozonolysis of 2-Methyl-2-undecen-5-one *N,N*-Dimethylhydrazone (7e):
Ozone is passed through a solution of **7e** (0.5 g, 2.1 mmol) in EtOAc (100 mL) at −60°C until the solution turns blue. The reaction vessel is flushed with nitrogen and Lindlar catalyst (0.025 g) is added. An atmosphere of hydrogen (1 atm) is maintained until its uptake is complete. The catalyst is removed by filtration through a bed of celite and following removal of the solvent, distillation gives **5e**; yield: 0.27 g (86%).

Methyl 13-Methyl-9-oxo-12-tetradecenoate (4g):
The imine **2** (3.10 g, 0.015 mol) is alkylated with methyl 7-bromoheptanoate[29] (4.01 g, 0.018 mol) as described above. The crude alkylation mixture is dissolved in benzene (120 mL) and is added to 1% aqueous oxalic acid (260 mL).[15] The mixture is stirred vigorously at r.t. until IR analysis indicates that hydrolysis of the imine is complete (22 h). The aqueous layer is extracted with Et_2O (2 × 50 mL), and the combined organic layers are washed with 1% oxalic acid (20 mL), water (20 mL), sat. $NaHCO_3$ (2 × 10 mL), and brine (2 × 10 mL). After drying over Na_2SO_4 removal of the solvent gives **4g** as a yellow oil which is purified by fractional distillation; yield: 1.79 g (45%); bp 116–120°C/0.4 Torr; 88% pure by GLC (Carbowax 20M, 180°C). An analytically pure sample is obtained by preparative GLC (Carbowax 20M, 150°C).

$C_{16}H_{28}O_3$	calc.	C 71.60	H 10.50	
(268.40)	found	71.34	10.37	

IR (film): ν = 1739 (CO_2CH_3); 1711 (C=O); 833 cm^{-1} (olefinic C–H).

^{1}H-NMR ($CDCl_3$/TMS): δ = 1.3 (m, 10H); 1.61 (s, 3H); 1.66 (s, 3H); 2.26–2.41 (overlapping signals, 8H); 3.65 (s, 3H); 5.05 (br s, 1H).

^{13}C-NMR ($CDCl_3$/TMS): δ = 17.6, 22.5, 23.6, 24.8, 25.6, 28.9, 29.0, 34.0, 42.73, 42.67, 51.3, 51.4, 122.9, 132.5, 174.1, 210.9.

Methyl 9,12-Dioxododecanoate (5g) by Ozonolysis of 4g:
4g (13.4 g, 0.05 mol) is ozonized in EtOAc (100 mL), Me_2S (0.25 mol) being used as reducing agent. After evaporation of solvent, DMSO is removed by passing the crude product through a column of silica gel (eluent Et_2O) to give, after distillation, **5g**: yield: 11.3 g (93%); bp 140–142°C/0.1 Torr.

IR, ^{1}H-NMR spectroscopic data in agreement with those reported in Ref. 12.

^{13}C-NMR ($CDCl_3$/TMS): δ = 23.8, 24.9, 29.0, 34.1, 34.7, 37.5, 42.7, 51.5, 51.6, 174.3, 200.65, 208.9.

Methyl 13-Methyl-9-oxo-12-tetradecenoate *N,N*-Dimethylhydrazone (7g):
3 (7.8 g, 0.05 mol) is alkylated with methyl 7-bromoheptanoate (8.4 g, 0.05 mol) as described above. Distillation of the crude product gives **7g**; yield: 8.2 g (53%); bp 140–144°C/0.5 Torr.

$C_{18}H_{34}N_2O_2$	calc.	C 69.63	H 11.03	N 9.02
(310.5)	found	69.58	10.93	9.07

IR (film): ν = 1741 (CO_2CH_3); 1630 cm^{-1} (C=N).

^{1}H-NMR ($CDCl_3$/TMS): δ = 1.39 (m, 10H); 1.61 (s, 3H); 1.67 (s, 3H); 2.16–2.53 (overlapping signals, 8H); 2.39 (s, 6H); 3.66 (s, 3H); 5.11 (br s, 1H).

^{13}C-NMR ($CDCl_3$/TMS): δ = 24.8, 25.1, 25.6, 25.8, 27.05, 29.0, 29.2, 29.6, 29.7, 34.0, 35.85, 36.1, 47.45, 51.3, 123.4, 132.2, 172.0, 174.1.

Methyl 9,12-Dioxodecanoate (5g) by Ozonolysis of 7g:
7g (1.0 g, 3.18 mmol) is ozonized in EtOAc (48 mL) as before. The ozonide formed is reduced by hydrogenation in the presence of Lindlar catalyst, and the crude product is distilled to give **5g**; yield: 0.62 g (80%).

2-Methyl-2-dodecen-9-yn-6-one (4h):
The imine **2** (31.05 g, 0.15 mol) is alkylated with 1-bromo-2-pentyne[30] (26.46 g, 0.18 mol) and hydrolyzed with 10% HCl as described above. Distillation of the crude product gives **4h** as a colourless oil; yield: 22.0 g (77%); bp 94–96°C/0.8 Torr.

$C_{13}H_{20}O$	calc.	C 81.19	H 10.48
(192.3)	found	80.96	10.29

IR (film): ν = 2254 (C≡C); 1712 (C=O); 833 cm^{-1} (olefinic C–H).

^{1}H-NMR ($CDCl_3$/TMS): δ = 1.07 (t, 3H, J = 7.5 Hz); 1.59 (s, 3H); 1.65 (s, 3H); 2.1–2.6 (overlapping signals, 10H); 5.01 (br s, 1H).

^{13}C-NMR ($CDCl_3$/TMS): δ = 12.3, 13.4, 14.2, 34.7, 77.7, 81.75, 122.55, 132.2, 208.45.

(*Z*)-4-Oxo-7-decenal (5h):
Ozone (5.5 mmol) is passed through a gas dispersion tube into a solution of **4h** (1.0 g, 5.2 mmol) in MeOH (100 mL) at −60 °C. The ozonide formed is hydrogenated in the presence of quinoline (0.3 mL) and Lindlar catalyst (26 mg). The catalyst is removed by filtration through celite and, after evaporation of the solvent, distillation gives **5h**; yield: 0.83 g (96%); bp 80–82 °C/0.4 Torr.

IR, ^{1}H-NMR spectroscopic data in agreement with those reported in Ref. 23.

^{13}C-NMR ($CDCl_3$/TMS): δ = 14.3, 20.5, 21.6, 34.7, 37.4, 42.6, 126.9, 132.9, 200.5 207.25.

2-[(*Z*)-2-Pentenyl]-2-cyclopenten-1-one (6h):
5h (1.66 g, 0.01 mol) is stirred in a mixture of 1% NaOH (44 mL) and Et_2O (66 mL); the reaction is monitored by GLC and is complete after 24 h. Distillation of the crude product gives **6h**; yield: 1.27 g (87%); bp 64–66 °C/0.05 Torr.

IR, ^{1}H-NMR spectroscopic data in agreement with those reported in Ref. 23.

2-Methyl-2-dodecen-9-yn-6-one *N,N*-Dimethylhydrazone (7h):
3 (7.8 g, 0.5 mmol) is alkylated with 1-bromo-2-pentyne (7.35 g, 0.05 mol) to give, after distillation, **7h**; yield: 7.5 g (64%); bp 96–108 °C/2 Torr.

$C_{15}H_{26}N_2$	calc.	C 76.86	H 11.18	N 11.95
(234.4)	found	76.77	10.98	11.83

IR (film): ν = 2253 (C≡C); 1631 cm^{-1} (C=N).

^{1}H-NMR ($CDCl_3$/TMS): δ = 1.06 (t, 3H, J = 5.4 Hz); 1.59 (s, 3H); 1.66 (s, 3H); 2.13–2.58 (overlapping signals, 10H); 2.37 (s, 6H); 5.07 (br s, 1H).

^{13}C-NMR ($CDCl_3$/TMS): δ = 12.3, 14.1, 14.2, 16.1, 16.6, 25.0, 25.6, 29.3, 30.15, 35.2, 36.0, 47.4, 78.0, 82.5, 123.3, 131.9, 170.8.

The financial support of the University College, Galway, Research Development Fund is gratefully acknowledged.

Received: 19 January 1989

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