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Jack E. Baldwin [a] , Gareth J. Pritchard [a] & Richard E. Rathmell [a]
[a] Dyson Perrins Laboratory, South Parks Road, Oxford, OX1 3QY, UK
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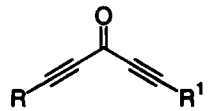
SYNTHESIS OF NOVEL UNSYMMETRICAL AND SYMMETRICAL DIACETYLENIC KETONES.

Jack E Baldwin,* Gareth J Pritchard and Richard E Rathmell.

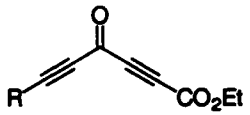
Dyson Perrins Laboratory, South Parks Road, Oxford, OX1 3QY, UK

Abstract: A convenient and efficient method for the preparation of unsymmetrical and symmetrical diacetylenic ketones bearing a carboxylate group.

Following on from our initial studies into the use of alkynyl ketones in the synthesis of novel heterocycles[1] we found it interesting to synthesise a range of diacetylenic ketones of the type **3**. Whilst symmetrical[2] **1** and unsymmetrical[3] **2** diacetylenic ketones have been reported in the literature there are no reports of unsymmetrical diynones bearing an ester group at the terminus of one of the triple bonds **3** (Figure 1). We now wish to report the facile synthesis of a novel range of diacetylenic ketones of the type **3** in good yield.



1 R = R^1 = alkyl / aryl
2 R ≠ R^1 = alkyl / aryl



3 R = alkyl / aryl or carboxylate

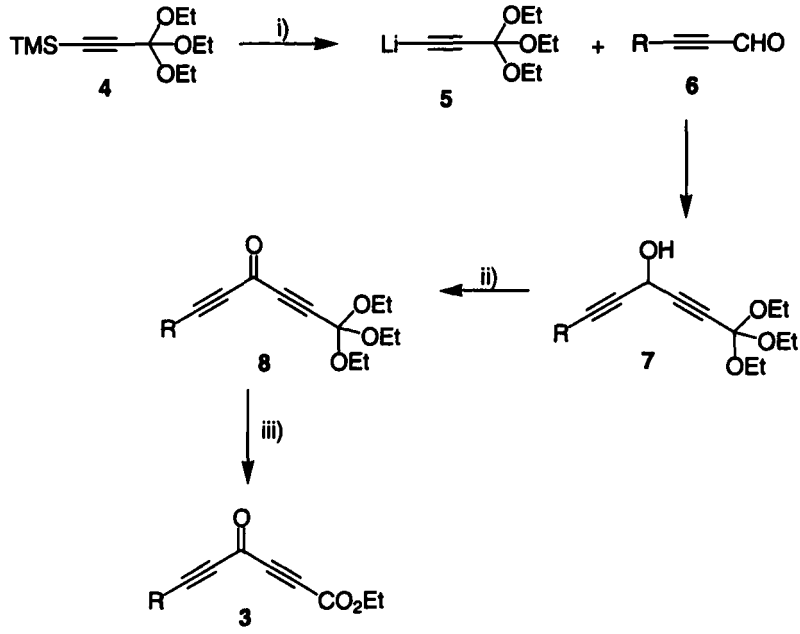
Figure 1

* To whom the correspondence should be addressed; Email: Jack.Baldwin@chem.ox.ac.uk.

Retrosynthetic analysis of **3** shows it may be possible for the addition of a metallo propiolate to an appropriate aldehyde, with subsequent oxidation of the intermediate alcohol to generate structure of the type. Whilst lithio propiolates have been reported previously[4] we have found that sluggish reactivity and unwanted side reaction (notably 1,4 addition to the conjugated system) have hampered the rapid synthesis of **3**. We have also found problems accessing **3** through palladium-catalysed reactions of tetraorganotin reagents with the appropriate acyl chloride,[5] or copper(I) acetylide-acyl chloride strategies.[6] We have also found that the presence of the ester group caused problems during the oxidation of the secondary alcohol to ketone. We believe that compounds such as **3** are highly reactive species and may be being generated *in situ* from the oxidation reactions and palladium cross couplings, but the reaction condition involved in the formation are causing decomposition of material before isolation is possible. We also believe that the carboxylate functionality was somehow causing problems during the oxidation, we therefore sought a suitable carboxylate protecting group which would be stable to the reaction conditions. This has directed us to develop a very mild synthesis of **3** using a protected carboxylate function.

Boche has reported the use of lithium ethyl orthopropiolate **5** as an easy to handle propiolate anion equivalent.[7] Herein we report the use of this protected carboxylate group in the synthesis of **3** (Scheme 1).

Treatment of **4** with *n*-butyllithium at 0 °C cleanly generates the anion **5**,[7] slow addition of the aldehydes **6**[8] resulted in the formation of the alcohols **7** in



Scheme 1 *Reagents and Conditions*: i) *n*-BuLi, THF, 0 °C; ii) MnO_2, benzene, room temperature; iii) Amberlyst 15™, benzene, room temperature, 15 mins,

Table 1

excellent yield. Further treatment of **7** with freshly prepared activated manganese dioxide[9] in benzene provided the ketones.

It is important to note that to keep the high yields and product purity the oxidant must be freshly prepared, commercially available sources of this reagent gave variable results. Deprotection of ortho esters is known using either *p*-TsOH[10] or PPTS.[11] However, we anticipated that compound **3** would be highly reactive, thus limiting methods for deprotection. Indeed, when using *p*-TsOH, we have found that due to difficulties in product purification, **3** was always contaminated with

Table 1

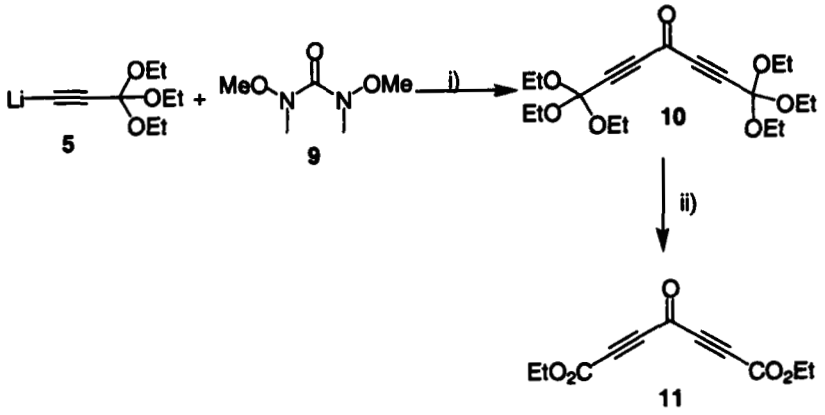
Entry	R	Yield of 7[(i)] %	Yield of 3[(ii)] %
1	Ph	74	94
2	*n*-Pr	76	98
3	*n*-Bu	80	95

(i) Isolated yield after chromatography; (ii) Yield after two steps, compounds **7** are highly reactive and attempts to purify them resulted in total decomposition of material. However samples were essentially pure by ^{13}C and ^{1}H NMR.

acid. However, we have found that **8** can be deprotected readily using the strong acid cation exchange resin Amberlyst 15™ to afford the desired ethyl esters **3** in good overall yield; the use of the resin allowed easy removal by filtration, resulting in almost pure material (Table 1).

Although conversion of **7** to **3** can be achieved by a sequential process, we have found that isolation of **8** is unnecessary and direct deprotection of **8** results directly in **3** in excellent overall yield.

Preparation of the symmetrical diethyl ester **3** (R = CO_2Et) was achieved as follows. Reich has reported the use of *N,N'*-dimethoxy-*N,N'*-dimethyl urea **9** as a carbonyl equivalent in the preparation of symmetrical aryl acetylenic ketones.[12,13] Treatment of the urea **9** with two equivalents of lithio ethyl orthopropiolate ester **5** at low temperature resulted in a moderate yield of the di-protected ester **10**.



Scheme 2 *Reagents and Conditions*: i) THF, -78 °C, (**10**, 36%); ii) Amberlyst 15™, benzene, room temperature, (**11**, 95%).

Subsequent treatment with Amberlyst 15™ resin afforded the desired diethyl ester **11**[14] in good yield (Scheme 2).

In summary we have demonstrated that a range of novel, highly reactive diacetylenic ketones can be readily and easily synthesised in good yield. The scope and limitations of the use of these reagents in heterocycle synthesis will be reported in due course.

General Experimental

Preparation of trimethylsilyl orthopropiolate triethylester **4**[7]*: n*-butyllithium (13 cm^3, of a 1.92 M solution in Hexanes, 2.5 mmol) was added dropwise to a stirred solution of trimethylsilyl acetylene (2.5 g, 2.5 mmol) in dry ether (30 cm^3) at 0 °C under argon. This solution was stirred for 1 hr before being cooled to –78 °C

and triethoxycarbenium tetrafluoroborate[15] (6.00 g, 2.5 mmol) added. The mixture was allowed to stir at this temperature for a further hour before being allowed to warm to room temperature. After this time K_2CO_3 (sat., 100 cm^3) was added, and the mixture extracted with ether (3 x 100 cm^3). The combined organic extracts were dried ($MgSO_4$) and the solvent removed *in vacuo*. The residue was purified by distillation to yield a colourless oil (5.01 g, 80%); b.p. 100 °C @ 13mmHg; ν_{max} (Film)/cm^{-1} 3040 (CH), 2860 (CH), 2115 (C≡C), 1440, 1250, 1230; δ_H (200 MHz, $CDCl_3$) 4.41 (6H, q, J = 7Hz, OCH_2CH_3), 1.22 (9H, t, J = 7Hz, OCH_2CH_3), 0.18 (9H, s, $Si(CH_3)_3$); δ_C (50.3 MHz, $CDCl_3$) 108.33 ($C(OC_2H_5)_3$), 98.54 (C≡), 88.81 (C≡), 58.89 (CH_2), 14.85 (CH_3), -0.35 ($Si(CH_3)_3$); *m/z* (Cl^+, NH_3) 200 (100%, MH^+ - OC_2H_5); (Found: MH^+ 245.1498, $C_{12}H_{25}SiO_3$ requires MH^+, 245.1494);

General Preparation of hydroxy alkynoate ortho esters: *n*-Butyllithium (1.0 eq) was a added dropwise to a stirred solution of trimethylsilyl orthopropiolate triethylester **4** (1.0 eq) at 0 °C in dry THF (2 cm^3 / 100 mg) under argon. The resulting solution was stirred at this temperature for 1 hr, after this time the aldehyde (1.1 eq) in dry THF (1 cm^3 / 100 mg) was added *via* syringe pump over 30 mins. The resulting solution was stirred for a further 2 hrs before ammonium chloride (sat. 0.5 cm^3 / 1 cm^3 of solvent) was added. The organic phase was separated and washed with water (10 cm^3) the combined aqueous washings were extracted with ether (3 x 20 cm^3). The combined organic extracts were dried

($MgSO_4$) and the solvent removed *in vacuo*. Purification of the product was accomplished by flash chromatography.

6,6,6-Triethoxy-1-phenyl-1,4-hexadiyn-3-ol **7** (R = Ph)**:** Treatment of **4** (560 mg, 0.229 mmol) with *n*-butyllithium (1.05 cm^3, of a 2.2 M solution in Hexanes, 0.229 mmol) in THF (11 cm^3) and then phenylpropargyl aldehyde (327 mg, 0.251 mmol) in THF (3.3 cm^3), as described above, and subsequent flash chromatography (light petroleum:EtOAc [10:1]) gave **7** (R = Ph) as a pale yellow oil (511 mg, 74%); R_f = 0.21 [light petroleum:EtOAc (10:1)]; ν_{max} (Film)/cm^{-1} 3425 (OH), 2979 (CH), 2899 (CH), 2237 (C≡C); δ_H (200 MHz, $CDCl_3$) 7.47-7.31 (5H, m, Ar), 5.42 (1H, s, CC*H*(OH)C), 3.70 (6H, q, *J* = 7Hz, OCH_2CH_3), 2.78 (1H, bs, OH), 1.25 (9H, t, *J* = 7Hz, OCH_2CH_3); δ_C (50.3 MHz, $CDCl_3$) 132.11 (CH), 128.21 (CH), 128.10 (CH), 122.30 (C), 108.62 ($C(OC_2H_5)$), 87.44 (C≡), 83.83 (C≡), 78.29 (C≡), 75.87 (C≡), 54.52 (CH), 50.22 (CH_2), 14.13 (CH_3); *m/z* (Cl^+, NH_3) 257 (100%, MH^+ - OC_2H_5); (Found: MH^+ 303.1523. $C_{18}H_{23}O_4$ requires MH^+, 303.1518).

9,9,9-Triethoxy-4,7-hexadiyn-6-ol **7** (R = ^{n}Pr)**:** Treatment of **4** (2.3 g, 12.9 mmol) with *n*-butyllithium (5.0 cm^3, of a 2.2 M solution in Hexanes, 12.9 mmol) in THF (56 cm^3) and then hex-2-ynal (1.2 g, 14.9 mmol) in THF (12 cm^3), as described above, and subsequent flash chromatography (light petroleum:EtOAc [10:1]) gave **7** (R = ^{n}Pr) as a colourless oil (2.62 g, 76%); R_f = 0.31 [light petroleum:EtOAc (10:1)]; ν_{max} (Film)/cm^{-1} 3438 (OH), 2977 (CH), 2934 (CH),

2238 (C≡C); δ_H (200 MHz, $CDCl_3$) 5.15 (1H, s, CC*H*(OH)C), 3.65 (6H, q, *J* = 7Hz, OCH_2CH$_3$), 2.61 (1H, bs, OH), 2.17 (2H, t, *J* = 7Hz, CH_2C≡), 1.50 (2H, sextet, *J* = 7Hz, CH_2CH$_3$), 1.25 (9H, t, *J* = 7Hz, OCH$_2$CH_3), 0.91 (3H, t, *J* = 7Hz, CH_3CH$_2$CH$_2$); δ_C (50.3 MHz, $CDCl_3$) 108.62 (*C*(OC_2H_5)), 85.87 (C≡), 81.76 (C≡), 77.92 (C≡), 76.88 (C≡), 58.97 (CH), 50.08 (CH_2), 21.62 (CH_2), 20.53 (CH_2), 14.75 (CH_3), 13.31 (CH_3); *m/z* (Cl^+, NH_3) 224 (100%, MH^+ - OC_2H_5); (Found: MH^+ 269.1682, $C_{15}H_{25}O_4$ requires *MH*$^+$, 269.1674).

10,10,10-Triethoxy-5,8-hexadiyn-7-ol **7** (R = ^{n}Bu)**:** Treatment of **4** (2.00 g, 8.19 mmol) with *n*-butyllithium (4.2 cm^3, of a 1.92 M solution in Hexanes, 8.19 mmol) in THF (40 cm^3) and then hept-2-ynal (991 mg, 9.0 mmol) in THF (10 cm^3), as described above, and subsequent flash chromatography (light petroleum:EtOAc [10:1]) gave **7** (R = ^{n}Bu) as a colourless oil (1.84 g, 80%); R_f = 0.32 [light petroleum:EtOAc (10:1)]; ν_{max} (Film)/cm^{-1} 3436 (OH), 2928 (CH), 2934 (CH), 2239 (C≡C); δ_H (200 MHz, $CDCl_3$) 5.17 (1H, s, CC*H*(OH)C), 3.66 (6H, q, *J* = 7Hz, OCH_2CH$_3$), 2.38 (1H, bs, OH), 2.25-2.17 (2H, m, CH_2C≡), 1.51-1.40 (4H, m, CH_2CH_2), 1.38 (9H, t, *J* = 7Hz, OCH$_2$CH_3), 0.95 (3H, t, *J* = 7Hz, CH_3CH$_2$CH$_2$); δ_C (50.3 MHz, $CDCl_3$) 108.64 (*C*(OC_2H_5)), 86.10 (C≡), 81.71 (C≡), 77.89 (C≡), 76.71 (C≡), 58.99 (CH_2), 52.08 (CHOH), 30.21 (CH_2), 22.25 (CH_2), 18.30 (CH_2), 14.77 (CH_3), 13.48 (CH_3); *m/z* (Cl^+, NH_3) 236 (100%, MH^+ - OC_2H_5); (Found: MH^+ 283.1831, $C_{16}H_{27}O_4$ requires *MH*$^+$, 283.1831).

General Preparation of keto alkynoate ortho esters. Freshly prepared activated

manganese dioxide[9] (1 g / 100 mg of alcohol) was added in one portion to a stirred solution of the alcohol in dry benzene (10 cm^3 / 100 mg of alcohol). After completion of the reaction (tlc control) the solids were removed by filtration over celite™, the cake was washed with benzene (5 cm^3 / 100 mg) and the solvent was removed *in vacuo* to yield pure material.

6,6,6-Triethoxy-1-phenyl-1,4-hexadiyn-3-one **8** *(R = Ph):* MnO_2 (1.9 g) was added to the alcohol **7** (R = Ph) (187 mg, 0.617 mmol) in benzene (19 cm^3). The resultant suspension was stirred for 90 mins before the mixture was filtered and the solvent removed *in vacuo*, to give the ketone **8** (R = Ph) as a yellow oil (184 mg, 99%); R_f = 0.49 [light petroleum:EtOAc (10:1)]; ν_{max} (Film)/cm^{-1} 2984 (CH), 2204 (C≡C), 1631 (C=O); δ_H (200 MHz, $CDCl_3$) 7.62-7.36 (5H, m, Ar), 3.72 (6H, q, *J* = 7Hz, OCH_2CH_3), 1.24 (9H, t, *J* = 7Hz, OCH_2CH_3); δ_C (50.3 MHz, $CDCl_3$) 159.81 (C=O), 133.40 (CH), 131.52 (CH), 128.75 (CH), 119.05 (C), 108.73 ($C(OC_2H_5)$), 92.83 (C≡), 89.09 (C≡), 84.59 (C≡), 81.49 (C≡), 59.47 (CH_2), 14.79 (CH_3); *m/z* (Cl^+, NH_3) 256 (100%, MH^+ - OC_2H_5), 179 (42); (Found: MH^+ 301.1380, $C_{18}H_{21}O_4$ requires MH^+, 301.1361).

9,9,9-Triethoxy-4,7-hexadiyn-6-one **8** (R = ^{n}Pr): MnO_2 (2.0 g) was added to the alcohol **7** (R = ^{n}Pr) (200 mg, 0.746 mmol) in benzene (20 cm^3). The resultant suspension was stirred for 90 mins before the mixture was filtered and the solvent removed *in vacuo*, to give the ketone **8** (R = ^{n}Pr) as a yellow oil (196 mg, 99%); R_f = 0.49 [light petroleum:EtOAc (10:1)]; ν_{max} (Film)/cm^{-1} 2977 (CH), 2221

(C≡C), 1635 (C=O); δ_H (200 MHz, $CDCl_3$) 3.69 (6H, q, J = 7Hz, OCH_2CH_3), 2.38 (2H, t, J = 7Hz, $CH_2C\equiv$), 1.60 (2H, sextet, J = 6.8Hz, CH_3CH_2), 1.24 (9H, t, J = 7Hz, OCH_2CH_3), 0.98 (3H, t, J = 7Hz, $CH_3CH_2CH_2$); δ_C (50.3 MHz, $CDCl_3$) 158.11 (C=O), 108.62 ($C(OC_2H_5)$), 97.03 (C≡), 83.76 (C≡), 82.07 (C≡), 81.54 (C≡), 59.34 (CH_2), 20.98 (CH_2), 20.89 (CH_2), 14.67 (CH_3), 13.31 (CH_3); *m/z* (Cl^+, NH_3) 222 (100%, MH^+ - OC_2H_5); (Found: MH^+ 267.1682, $C_{15}H_{23}O_4$ requires MH^+, 267.1674).

10,10,10-Triethoxy-5,8-hexadiyn-7-one **8** (R = ^{n}Bu)**:** MnO_2 (2.0 g) was added to the alcohol **7** (R = ^{n}Bu) (200 mg, 0.709 mmol) in benzene (20 cm^3). The resultant suspension was stirred for 90 mins before the mixture was filtered and the solvent removed *in vacuo*, to give the ketone **8** (R = ^{n}Bu) as a yellow oil (197 mg, 99%); R_f = 0.50 [light petroleum:EtOAc (10:1)]; ν_{max} (Film)/cm^{-1} 2928 (CH), 2215 (C≡C), 1636 (C=O); δ_H (200 MHz, $CDCl_3$) 3.69 (6H, q, J = 7Hz, OCH_2CH_3), 2.40 (2H, t, J= 6.8Hz, $CH_2C\equiv$), 1.57-1.37 (4H, m, CH_2CH_2), 1.24 (9H, t, J = 7Hz, OCH_2CH_3), 0.91 (3H, t, J = 7Hz, $CH_3CH_2CH_2$); δ_C (50.3 MHz, $CDCl_3$) 158.12 (C=O), 108.71 ($C(OC_2H_5)$), 97.11 (C≡), 84.71 (C≡), 81.99 (C≡), 80.32 (C≡), 59.99 (CH_2), 44.96 (CH_2), 29.33 (CH_2), 18.78 (CH_2), 14.72 (CH_3), 13.38 (CH_3); *m/z* (Cl^+, NH_3) 234 (100%, MH^+ - OC_2H_5); (Found: MH^+ 281.1831, $C_{16}H_{27}O_4$ requires MH^+, 281.1831).

General Preparation of diacetylenic ester. Amberlyst 15™ (100 mg / 100 mg of ketone) was added in one portion to a stirred solution of the ketone in dry

benzene (10 cm^3 / 100 mg of ketone). After completion of the reaction (tlc control) the solids were removed by filtration over celite™, the cake was washed with benzene (5 cm^3 / 100 mg). The solvent was removed *in vacuo* to yield pure material.

Ethyl-1-phenyl-1,4-hexadiyn-3-on-5-oate **3** (R = Ph)**:** Amberlyst 15™ (184 mg) was added to the ketone **8** (R = Ph) (187 mg, 0.623 mmol) in benzene (19 cm^3). The resultant suspension was stirred for 60 mins before the mixture was filtered and the solvent removed *in vacuo*, to give the ketone **3** (R = Ph) as a yellow oil (139 mg, 99%); R_f = 0.50 [light petroleum:EtOAc (10:1)]; ν_{max} (Film)/cm^{-1} 2984 (CH), 2204 (C≡C), 1720 (CO_2Et), 1631 (C=O); δ_H (200 MHz, $CDCl_3$) 7.67-7.42 (5H, m, Ar), 4.32 (2H, q, *J* = 7Hz, OCH_2CH_3), 1.33 (3H, t, *J* = 7Hz, OCH_2CH_3); δ_C (50.3 MHz, $CDCl_3$) 159.81 (C=O), 151.99 (C=O), 133.61 (CH), 131.92 (CH), 128.75 (CH), 118.65 (C), 99.93 (C≡), 88.69 (C≡), 80.79 (C≡), 78.01 (C≡), 63.17 (CH_2), 13.79 (CH_3); *m/z* (Cl^+, NH_3) 182 (100%, MH^+ - OC_2H_5); (Found: MH^+ 227.0630, $C_{14}H_{11}O_3$ requires MH^+, 227.0629).

Ethyl-4,7-nonadiyn-6-on-8-oate **3** (R = ^{n}Pr)*:* Amberlyst 15™ (184 mg) was added to the ketone **8** (R = ^{n}Pr) (196 mg, 0.737 mmol) in benzene (19 cm^3). The resultant suspension was stirred for 60 mins before the mixture was filtered and the solvent removed *in vacuo*, to give the ketone **3** (R = ^{n}Pr) as a yellow oil (138 mg, 98%); R_f = 0.51 [light petroleum:EtOAc (10:1)]; ν_{max} (Film)/cm^{-1} 2969 (CH), 2211 (C≡C), 1723 (CO_2Et), 1635 (C=O); δ_H (200 MHz, $CDCl_3$) 4.33 (2H, q, *J* =

7Hz, OCH_2CH_3), 2.42 (2H, t, J = 7Hz, $CH_2C\equiv$), 1.63 (2H, sextet, J = 7Hz, CH_3CH_2), 1.30 (3H, t, J = 7Hz, OCH_2CH_3), 0.99 (3H, t, J = 7Hz, $CH_3CH_2CH_2$); δ_C (50.3 MHz, $CDCl_3$) 158.89 (C=O), 151.98 (C=O), 99.41 (C≡), 81.57 (C≡), 80.90 (C≡), 76.98 (C≡), 63.05 (CH_2), 21.12 (CH_2), 20.87 (CH_2), 13.86 (CH_3), 13.42 (CH_3); *m/z* (Cl^+, NH_3) 149 (100%, $MH^+ - OC_2H_5$); (Found: MH^+ 193.1682, $C_{15}H_{23}O_4$ requires MH^+, 193.1674).

Ethyl-5,8-decadiyn-7-on-9-oate **3** (R = ^{n}Bu): Amberlyst 15™ (200 mg) was added to the ketone **8** (R = ^{n}Bu) (196 mg, 0.70 mmol) in benzene (20 cm^3). The resultant suspension was stirred for 60 mins before the mixture was filtered and the solvent removed *in vacuo*, to give the ketone **3** (R = ^{n}Bu) as a yellow oil (141 mg, 98%); R_f = 0.51 [light petroleum:EtOAc (10:1)]; ν_{max} (Film)/cm^{-1} 2928 (CH), 2211 (C≡C), 1721 (CO_2Et), 1636 (C=O); δ_H (200 MHz, $CDCl_3$) 4.33 (2H, q, J = 7Hz, OCH_2CH_3), 2.42 (2H, t, J= 7Hz, $CH_2C\equiv$), 1.63-1.24 (7H, m, CH_2CH_2, OCH_2CH_3), 0.91 (3H, t, J = 7Hz, $CH_3CH_2CH_2$); δ_C (50.3 MHz, $CDCl_3$) 158.95 (C=O), 152.02 (C=O), 99.69 (C≡), 81.47 (C≡), 80.93 (C≡), 77.14 (C≡), 63.09 (CH_2), 29.28 (CH_2), 21.90 (CH_2), 18.32 (CH_2), 13.95 (CH_3), 13.42 (CH_3); *m/z* (Cl^+, NH_3) 162 (100%, $MH^+ - OC_2H_5$); (Found: MH^+ 207.1831, $C_{16}H_{27}O_4$ requires MH^+, 207.1831).

1,1,1-Triethoxy-6,6,6-triethoxy-2,6-heptadiyn-4-one **10**: *n*-Butyllithium (1.05 cm^3, of a 1.9 M solution in Hexanes, 2.0 mmol) was added dropwise at 0 °C to a stirred solution of trimethylsilyl orthopropiolate triethylester **4**[7] (500 mg, 2.0

mmol) in dry THF (10 cm^3) under argon. The resultant solution was allowed to warm to room temperature and stir for a further hour before being transferred *via* cannular into a solution of *N,N'*-dimethoxy-*N,N'*-dimethyl urea **9**[12] (136 mg, 1.0 mmol) in dry THF (20 cm^3) at –78 °C under argon. The resultant solution was allowed to stir at this temperature for 30 mins before being allowed to warm to room temperature and stir for a further hour. The mixture was diluted with ether (20 cm^3) and washed with water (4 x 10 cm^3). The organic phase was dried ($MgSO_4$) and the solvent removed *in vacuo*. The residue was purified by flash chromatography eluting silica gel with (light petroleum:Et_2O [20:1]) to give **10** as a pale yellow oil (110 mg, 30 %); R_f = 0.20 [light petroleum:Et_2O (20:1)]; ν_{max} (Film)/cm^{-1} 2928 (CH), 2211 (C≡C), 1647 (C=O); δ_H (200 MHz, $CDCl_3$) 3.67 (12H, q, *J* = 7Hz, OCH_2CH_3), 1.24 (18H, t, *J* = 7Hz, OCH_2CH_3); δ_C (50.3 MHz, $CDCl_3$) 158.88 (C=O), 108.56 ($C(OC_2H_5)$), 85.77 (C≡), 81.03 (C≡), 59.42 (CH_2), 14.66 (CH_3); *m/z* (Cl^+, NH_3) 194 (100%, MH^+ - 4 x OC_2H_5 + 4 x H^+); (Found: MH^+ 371.1991, $C_{19}H_{31}O_7$ requires MH^+, 371.1991).

Diethyl-2,6-heptadiyn-4-on-1,7-oate **11**: Amberlyst 15™ (150 mg) was added in one portion to a stirred solution of 1,1,1-triethoxy-6,6,6-triethoxy-2,6-heptadiyn-4-one **10** (110 mg, 0.297 mmol) in dry benzene (15 cm^3). The resultant suspension was stirred at room temperature for 30 mins before the solids were removed by filtration and the solvent removed *in vacuo* to yield a yellow oil (64 mg, 97%); R_f = 0.30 [light petroleum:Et_2O (20:1)]; ν_{max} (Film)/cm^{-1} 2928 (CH), 2223 (C≡C), 1725 (CO_2Et), 1655 (C=O); δ_H (200 MHz, $CDCl_3$) 4.32 (4H, q, *J* =

7Hz, OCH_2CH_3), 1.35 (6H, t, J = 7Hz, OCH_2CH_3); This compound gave unsatisfactory mass spectral data.

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