Functional Carbonates: Cyclic α-Methylene and β-Oxopropyl Carbonates from Prop-2-ynyl Alcohol Derivatives and CO_2

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The phosphine-catalysed synthesis of cyclic α-methylene carbonates **2** directly from prop-2-ynyl alcohol derivatives and CO_2 is described. These cyclic carbonates **2** are key intermediates for the selective access to β-oxopropyl carbonates **3** by reaction with alcohols under mild conditions, but in the presence of Et_3N or KCN as catalyst.

Carbonates are widely used as solvents, as precursors of transparent polycarbonate glasses,[1] and as an efficient protecting group for alcohols and diols of interest for the access to biological compounds.[2]

Alkenyl carbonates have been used for the synthesis of carbamates by simple reaction of amines with isopropenyl carbonates at 50–70 °C,[3] or with highly reactive α-methoxyvinyl carbonates at less than 20 °C.[4] The decomposition of allyl carbonates by palladium(0) complexes has led to mild catalytic conditions for the allylation of soft nucleophiles.[5,6] Palladium(0) complexes also activate alk-2-ynyl carbonates to give allenyl palladium(II) intermediates for the formation of buta-2,3-dienoates under alkoxycarbonylation conditions,[7] allenyl acetylenes by reaction with terminal alkynes[8] or 2,3-disubstituted propenes in the presence of carbonucleophiles.[9] On the other hand, cyclic carbonates are especially useful for the synthesis of functional compounds and polymers.[1] On being heated with alcohols in the presence of Et_3N, saturated cyclic alkylene carbonates are opened to provide carbonates and diols by double transcarbonation,[10] whereas with primary and secondary amines they give hydroxylated carbamates.[11] Furanones can be obtained from the thermal degradation of 4-(acylmethylene)-1,3-dioxolan-2-one derivatives at 150–200 C.[12]

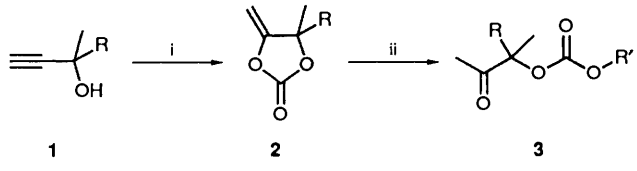
Simple dialkyl carbonates are usually synthesized from alcohols and chloroformates under basic conditions.[13] The opening of cyclic alkylene carbonates with alcohols in the presence of Et_3N is a useful industrial route to symmetrical dialkyl carbonates,[10] and activated cyclic carbonates allow the controlled formation of unsymmetrical carbonates.[14] Enol carbonates have been synthesized by reacting chloroformates with enolato mercury(II) derivatives,[3,4] or recently with an enolate generated from an aldehyde.[15]

Cyclic carbonates can be obtained from α-difunctional substrates. by phosgenation of diols[2,16] or α-hydroxy ketones.[17] Other methods are based on the transcarbonation of linear carbonates by diols,[18] the Co catalysed cyclisation of α-halo alcohols in the presence of CO_2,[19] the catalytic insertion of CO_2 into a C–O bond of an oxirane,[20,21] the allylic activation of vinylic oxiranes by Pd(0),[22] or the Rh(I) catalysed oxidation of styrene in the presence of oxygen and CO_2.[23]

Of special interest are the α-methylene carbonates which can be prepared by dehydrohalogenation of halomethyl species under UV irradiation [17a] or in the presence of a base.[24] Some of these carbonates have been synthesized starting from propargyl alcohol derivatives and CO_2 in the presence of metal catalysts such as Ru,[25] Co,[26] Pd [12,26,27] or Cu.[28] We have shown in a preliminary work [29] that some α-methylene carbonates of type **2** are very conveniently obtained in one step from propargyl alcohol derivatives and CO_2, but in the presence of catalytic amounts of a phosphine. We now wish to report: (i), a detailed study of this reaction and its extension to unsaturated α-alkynyl alcohols to afford functional polyunsaturated cyclic carbonates; and (ii), the use of these α-methylene cyclic carbonates **2** to selectively produce β-oxopropyl carbonates **3** (Scheme 1).

Table 1 Synthesis of α-methylene cyclic carbonates at 100 °C

Alcohol	Substituents	Time/h	Carbonate	Yield (%)
1a	$R^1 = R^2 = Me$	8	**2a**	98
1b	$R^1 = Me, R^2 = Et$	8	**2b**	98
1c	$R^1 = Me, R^2 = Bu^n$	20	**2c**	78
1d	$R^1 = Me, R^2 = Ph$	20	**2d**	32
1e	$R^1,R^2 = -[CH_2]_5-$	8	**2e**	58

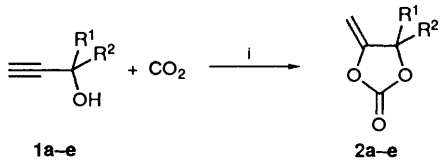


1 **2** **3**

Scheme 1 *Reagents:* i, CO_2; ii, R'OH

Results and Discussion

Cyclic α-Methylene Carbonates from Prop-2-ynyl Alcohols and Carbon Dioxide.—α-Alkynyl alcohol derivatives **1a–e** react under 5 MPa CO_2 pressure in the presence of a catalytic amount of tributylphosphine (0.2 equiv.) at 100 °C without a solvent to afford cyclic carbonates **2a–e** in good yields (Scheme 2) (Table 1).



1a–e **2a–e**

Scheme 2 *Reagent:* i, PBu_3

The formation of cyclic carbonates strongly depends on the nature of R^1 and R^2. No cyclic carbonates are formed starting from propargyl alcohol itself or secondary alkynyl alcohols and consequently the reaction appears to be specific for tertiary alcohols. The reaction is easily performed when R^1 and R^2 are linear alkyl groups (**2a**, **2b**, **2c**), but gave lower yields when one of these groups is bulky (**2e**) or unsaturated (**2d**).

Phosphines other than PBu_3 were tested as catalysts but they showed a lower activity. At 140 °C, 4,4-dimethyl-5-methylene-

Table 2 Formation of the cyclic carbonate **2a** from **1a** and CO_2[a]

Catalyst	Temp. (°C)	Time (h)	Yield (%)
PBu_3	140	20	86
	100	8	98
	50	20	97
PPh_3	140	20	78
	100	8	7
PCy_3	140	20	97
	100	8	8

[a] General conditions: alcohol **1a** (50 mmol), phosphine (4 mmol) and CO_2 (5 MPa).

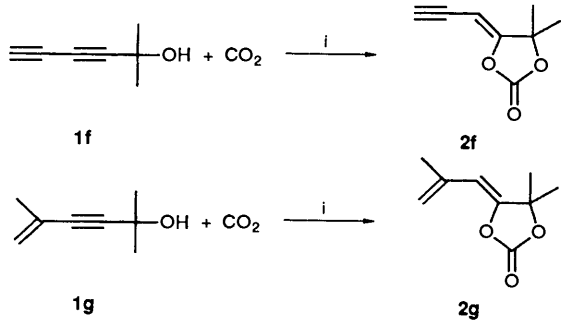
Table 3 Synthesis of β-oxopropyl carbonates **3** ($R^1 = R^2 = Me$)[a]

ROH	Temp. (°C)	Carbonate	Yield (%)
MeOH	0	**3a**	91
EtOH	20	**3b**	77
$PhCH_2OH$	20	**3d**	86
$CH_2{=}CHCH_2OH$	40	**3e**	67
$MeCOCH_2OH$	20	**3f**	75
$HC{\equiv}CCH(Me)OH$	20	**3g**	90

[a] General conditions: cyclic carbonate **2a** (10 mmol), alcohol (5 cm^3) and Et_3N (1 cm^3, 7 mmol).

1,3-dioxolan-2-one **2a** was isolated in 78 and 97% yield in the presence of triphenylphosphine and tricyclohexylphosphine, respectively, whereas only 7–8% yields were obtained with these phosphines at 100 °C (Table 2). PBu_3 is a much more efficient catalyst since a complete conversion of **1a** into **2a** is obtained by carrying out the reaction at 100 °C for 8 h or at 50 °C for 20 h. It must be pointed out that this phosphine-catalysed reaction is completely inhibited in the presence of a solvent such as toluene or THF.

The formation of the cyclic carbonate is not possible with a substituted prop-2-ynyl alcohol derivative such as $Me{-}C{\equiv}C{-}C(Me)_2OH$ or $Bu^n{-}C{\equiv}C{-}C(Me)_2OH$. However, it is noteworthy that if the substituent is an unsaturated conjugated group, the corresponding carbonate can be obtained. Thus 2-methylhexa-3,5-diyn-2-ol **1f**, and 2,5-dimethylhex-5-en-3-yn-2-ol **1g** reacted with CO_2 in the presence of PBu_3 to give the unsaturated carbonates **2f** and **2g** in 54 and 47% yields, respectively (Scheme 3).

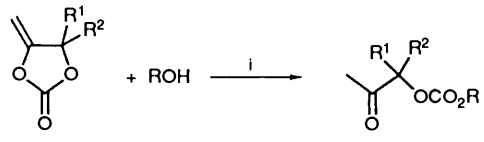


Scheme 3 *Reagent:* i, PBu_3(cat)

According to the reaction time and temperature, the phosphine was partially converted into phosphine oxide, but $OPBu_3$ was shown not to be the catalyst of this synthesis. The catalytic species could be the phosphine itself as it is able to activate triple bonds of acetylenic compounds such as acetylene mono- or di-carboxylates towards nucleophilic addition *via* vinyl phosphonium intermediates.[30] The basicity of the trialkyl phosphine may help the deprotonation of the alcohol before incorporating CO_2, but this base effect alone cannot explain the cyclisation since basic amines such as Et_3N are not catalysts for this reaction.

β-Oxopropyl Carbonates from 5-Methylene-1,3-dioxolan-2-ones.—Cyclic alkylene carbonates are known to react with alcohols to provide symmetrical[10] or unsymmetrical carbonates[14] by double transcarbonation, but the reactivity of α-methylene cyclic carbonates with alcohols is not described. Our first investigations showed the inertness of cyclic carbonates **2** with alcohols even in refluxing alcohols. However, a reaction occurred between the α-methylene carbonate **2a** and alcohols, but in the presence of a catalytic amount of PBu_3 at 140 °C for 20 h, leading to β-oxopropyl alkyl carbonates. Thus were obtained 1,1-dimethyl-2-oxopropyl methyl (**3a**), ethyl (**3b**) and isopropyl (**3c**) carbonates in 24, 47 and 47% yields, respectively, from 4,4-dimethyl-5-methylene-1,3-dioxolan-2-one **2a**.

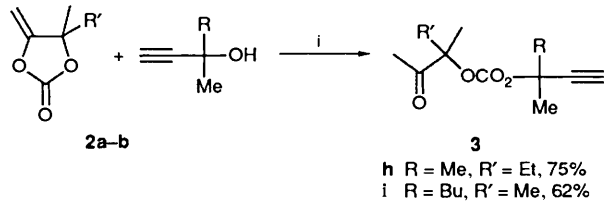
These drastic reaction conditions were modified into very mild ones, simply by using a tertiary amine catalyst in place of the phosphine (Scheme 4).



Scheme 4 *Reagents and conditions:* i, NEt_3(cat), 4–20 h, 0–40 °C

In the presence of a catalytic amount of triethylamine, carbonate **2a** slowly reacted at 20 °C until complete conversion (detected by GLC) to afford β-oxopropyl carbonate derivatives **3b**, **3d–f** from primary alcohols and **3g** from a functional secondary alcohol (Table 3). This reaction is very selective since no 3-hydroxyprop-1-en-2-yl carbonate derivatives resulting from the splitting of the other C–O carbonate bond were formed. Keto alcohols also reacted in the presence of the tertiary amine to yield di(β-oxopropyl) carbonate derivatives **3f**. The opening of this $O{-}(CO_2CMe_2)$ bond generates an enolate which on protonation by the alcohol gives an acetyl group. The β-oxopropyl carbonates thus formed are very stable since no further transcarbonation by an excess of alcohol, leading to symmetrical carbonates occurs, as is the case when alkylene carbonates are treated in the presence of Et_3N at 70–150 °C.[10]

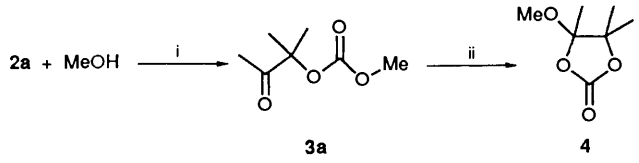
Tertiary alcohols failed to react under these experimental conditions even at 60 °C, but the use of KCN as catalyst made this reaction possible and the carbonates **3h** and **3i** could be obtained at 20 °C (Scheme 5). This simple reaction allows the



Scheme 5 *Reagents and conditions:* i, KCN(cat), 20 °C

formation of carbonates containing both the CH_3CO and $HC{\equiv}C$ functional groups. The utilization of KCN as catalyst was motivated by its use to activate esters for acylation.[31] The fact that KCN is a catalyst shows that the most important factor is the activation of the carbonyl and that even if NEt_3 is able to deprotonate the alcohol, KCN and Et_3N both act as carbonation catalysts.

In this reaction, methanol appears as a special case, since carbonate **3a** cannot be obtained under the above conditions at 20 °C. Actually, methanol reacts with 4,4-dimethyl-5-methylene-1,3-dioxolan-2-one in the presence of Et_3N or KCN at room temperature to afford 4-methoxy-4,5,5-trimethyl-1,3-dioxolan-2-one **4** in 61% yield. However, when the reaction is carried out at 0 °C, the opened carbonate **3a** is formed in quantitative yield. After isolation, the carbonate **3a** is stable in methanol, but in the presence of NEt_3 at room temperature it is converted into the carbonate **4** (Scheme 6).



Scheme 6 *Reagents and conditions:* i, NEt_3, 0 °C; ii, NEt_3, 20 °C

Conclusions

The mild phosphine-catalysed formation of α-methylene cyclic carbonates **2** in good yield allows the access to new functional β-oxopropyl carbonates, in only two steps from easily prepared prop-2-ynyl alcohol derivatives and CO_2.

The direct use of CO_2 for these syntheses of functional cyclic α-methylene and β-oxopropyl carbonates also represents an advantage over the classical use of chloroformates, the phosgene derivatives, for the search of new reactions involving non-harmful chemicals.

Experimental

^1H NMR spectra were recorded on a Bruker AW 80 (80 MHz) or a Bruker AC 30 WPB (300 MHz); *J*-values are in Hz. Mass spectra were performed with a Varian Mat 311 at the CRMPO, Rennes (France) and elemental analyses were carried out by the CNRS, Vernaison (France).

Prop-2-ynyl alcohol derivatives **1a–b** and **1d–e** were commercially available and used without further purification. Compounds **1c**, **1f** and **1g** were prepared from lithium acetylide and the appropriate ketone, according to a general method described by Brandsma.[32]

Synthesis of Cyclic Carbonates.—The prop-2-ynyl alcohol derivative (20 mmol) and tributylphosphine (1.6 mmol) were stirred for 8–20 h (see Table 1) at 100 °C under CO_2 pressure (5 MPa). The carbonates **2a–g** were isolated by distillation under reduced pressure (1–20 mmHg) or recrystallized.

4,4-*Dimethyl*-5-*methylene*-1,3-*dioxolan*-2-*one* **2a**. White solid (2.48 g, 97%) distilled under reduced pressure (20 mmHg, b.p. 80–82 °C), m.p. 25–30 °C; δ_H(80 MHz; $CDCl_3$) 4.72 (1 H, d, ^2J 4.0, CH_2=), 4.34 (1 H, d, ^2J 4.0, CH_2=) and 1.59 (6 H, s, Me_2C); ν/cm^{-1} 1827 (C=O) and 1687 (C=C) (Found: C, 55.98; H, 6.64. $C_6H_8O_3$ requires C, 55.98; H, 6.25%).

4-*Ethyl*-4-*methyl*-5-*methylene*-1,3-*dioxolan*-2-*one* **2b**. Colourless liquid (2.61 g, 92%) distilled under reduced pressure (1.5 mmHg, b.p. 55–60 °C); δ_H(300 MHz; $CDCl_3$) 4.73 (1 H, d, ^2J 3.8, CH_2=), 4.34 (1 H, d, ^2J 3.8, CH_2=), 1.82 (2 H, m, MeCH_2), 1.55 (3 H, s, Me) and 0.86 (3 H, t, ^2J 7.4, *Me*CH_2); ν/cm^{-1} 1832 (C=O) and 1688 (C=C) (Found: C, 59.15; H, 7.04. $C_7H_{10}O_3$ requires C, 59.36; H, 7.26%).

4-*Butyl*-4-*methyl*-5-*methylene*-1,3-*dioxolan*-2-*one* **2c**. Colourless liquid (2.65 g, 78%) distilled under reduced pressure (0.5 mmHg, b.p. 65–67 °C); δ_H(300 MHz; $CDCl_3$) 4.80 (1 H, d, ^2J 3.8, CH_2=), 4.29 (1 H, d, ^2J 3.8, CH_2=), 1.89–1.65 (2 H, m, CH_2C–O), 1.41–1.33 (4 H, m, [CH_2]$_2$Me), 1.54 (3 H, s, Me) and 0.89 (3 H, t, ^3J 6.4, *Me*[CH_2]$_3$); ν/cm^{-1} 1828 (C=O) and 1684 (C=C).

4-*Methyl*-5-*methylene*-4-*phenyl*-1,3-*dioxolan*-2-*one* **2d**. White solid (1.21 g, 32%) distilled under reduced pressure (1.5 mmHg, b.p. 126–128 °C); m.p. 25–30 °C; δ_H(80 MHz; $CDCl_3$) 7.40 (5 H, m, Ph), 4.90 (1 H, d, ^2J 3.2, CH_2=), 4.42 (1 H, d, ^2J 3.2, CH_2=) and 1.55 (3 H, s, Me); ν/cm^{-1} 1835 (C=O) and 1700 (C=C) (Found: C, 69.47; H, 5.26. $C_{11}H_{10}O_3$ requires C, 69.07; H, 5.58%).

5′-*Methylenecyclohexanespiro*-4′-(1′,3′-*dioxolan*)-2′-*one* **2e**. Colourless liquid (1.95 g, 58%) distilled under reduced pressure (1.0 mmHg, b.p. 80–85 °C); δ_H(80 MHz; $CDCl_3$) 4.72 (1 H, d, ^2J 4.0, CH_2=), 4.25 (1 H, d, ^2J 4.0, CH_2=) and 2.1–1.1 (10 H, m, spirocyclohexane); ν/cm^{-1} 1845 (C=O) and 1700 (C=C) (Found: C, 64.29; H, 7.14. $C_9H_{12}O_3$ requires C, 64.26; H, 7.21%).

4,4-*Dimethyl*-5-(*prop*-2-*ynylidene*)-1,3-*dioxolan*-2-*one* **2f**. White solid (1.64 g, 54%) recrystallized from a methanol–ether–hexane mixture, m.p. 129–130 °C; δ_H(80 MHz; $CDCl_3$), 4.76 (1 H, d, ^4J 3.8, =CH), 3.12 (1 H, d, ^4J 3.8, ≡CH) and 1.59 (6 H, s, Me_2C); ν/cm^{-1} 3290 (≡C–H), 1840 (C=O) and 1705 (C=C) (Found: C, 63.07; H, 5.49%; M$^+$, 152.047. $C_8H_8O_3$ requires C, 63.16; H, 5.26%; *M*, 152.048).

4,4-*Dimethyl*-5-(2-*methylprop*-2-*enylidene*)-1,3-*dioxolan*-2-*one* **2g**. White solid (1.58 g, 47%) recrystallized from an ether–hexane mixture, m.p. 35–40 °C; δ_H(80 MHz; $CDCl_3$) 5.12 (1 H, s, =CH), 4.98 (2 H, m, =CH_2), 2.00 (3 H, s, =C–Me) and 1.57 (6 H, s, Me_2C); ν/cm^{-1} 1825 (C=O) and 1705 (C=C) (Found: C, 64.08; H, 6.79%; M$^+$, 168.079. $C_9H_{12}O_3$ requires C, 64.26; H, 7.21%; *M*, 168.079).

Reaction with Alcohols.—*Method A*. 4,4-Dimethyl-5-methylene-1,3-dioxolan-2-one **2a** (10 mmol) and the alcohol (50 mmol) were stirred for 20 h at 140 °C under carbon dioxide (1 MPa) in the presence of PBu_3 (4 mmol). The linear carbonates **3** were isolated by distillation under reduced pressure.

Method B. The cyclic carbonate (10 mmol), the alcohol (5 cm^3), and triethylamine (1 cm^3, 7 mmol) or potassium cyanide (**3h** and **3i**) (26 mg, 0.4 mmol), were stirred for 20 h at 0–40 °C (see Table 3). The linear carbonates **3** were isolated by distillation under reduced pressure (0.5–1.5 mmHg), chromatographed on a silica column, or recrystallized.

1,1-*Dimethyl*-2-*oxopropyl methyl carbonate* **3a**. Method B (20 h at 0 °C) colourless liquid (1.46 g, 91%); distilled under reduced pressure (1.5 mmHg, b.p. 55–58 °C); δ_H(80 MHz; $CDCl_3$) 3.76 (3 H, s, MeO), 2.14 (3 H, s, MeCO) and 1.49 (6 H, s, Me_2C); ν/cm^{-1} 1765 and 1740 (C=O) (Found: C, 53.21; H, 7.90. $C_7H_{12}O_4$ requires C, 52.49; H, 7.55%).

1,1-*Dimethyl*-2-*oxopropyl ethyl carbonate* **3b**. Method B colourless liquid (1.34 g, 77%); distilled under reduced pressure (1.5 mmHg, b.p. 60 °C); δ_H(300 MHz; $CDCl_3$) 4.13 (2 H, q, ^3J 7.1, CH_2Me), 2.11 (3 H, s, *Me*CO), 1.45 (6 H, s, Me_2C) and 1.26 (3 H, t, ^3J 7.1, CH_2*Me*); ν/cm^{-1} 1743 and 1725 (C=O) (Found: C, 55.04; H, 8.02%; M$^+$, 174.090. $C_8H_{14}O_4$ requires C, 55.15; H, 8.10%; *M*, 174.089).

1,1-*Dimethyl*-2-*oxopropyl isopropyl carbonate* **3c**. Method A colourless liquid (0.88 g, 47%); distilled under reduced pressure (1.5 mmHg, b.p. 80–82 °C); δ_H(80 MHz; $CDCl_3$) 4.84 (1 H, hept, ^3J 6.0, C*H*Me_2), 2.14 (3 H, s, MeCO), 1.48 (6 H, s, Me_2C), 1.28 (6 H, d, ^3J 6.0, CH*Me*$_2$); ν/cm^{-1} 1745 and 1735 (C=O) (Found: C, 57.39; H, 8.95. $C_9H_{16}O_4$ requires C, 57.43; H, 8.57%).

Benzyl 1,1-*dimethyl*-2-*oxopropyl carbonate* **3d**. Method B colourless liquid (3.22 g, 86%); chromatographed on silica column using an ether–hexane mixture (1:9) as eluent; δ_H(300 MHz; $CDCl_3$) 7.32 (5 H, m, Ph), 5.08 (2 H, s, CH_2Ph), 2.09 (3 H, s, *Me*CO) and 1.47 (6 H, s, Me_2C); ν/cm^{-1} 1742 and 1725 (C=O) (Found: C, 66.15; H, 6.86; M$^+$, 236.104. $C_{13}H_{16}O_4$ requires C, 66.08; H, 6.82%; *M*, 236.105).

Allyl 1,1-*dimethyl*-2-*oxopropyl carbonate* **3e**. Method B colourless liquid (1.25 g, 67%); distilled under reduced pressure (0.7 mmHg, b.p. 40 °C); δ_H(300 MHz; $CDCl_3$) 5.86 (1 H, m,

CH=), 5.38 (1 H, m, $=CH_2$), 5.22 (1 H, m, $=CH_2$), 4.55 (2 H, m, CH_2–C), 2.10 (3 H, s, Me–CO) and 1.44 (6 H, s, Me_2C); ν/cm^{-1} 1746 and 1727 (C=O) (Found: C, 58.36; H, 7.60; M^+, 186.089. $C_9H_{14}O_4$ requires C, 58.05; H, 7.58%; *M*, 186.089).

1,1-*Dimethyl*-2-*oxopropyl* 2-*oxopropyl carbonate* **3f**. Method B colourless liquid (1.51 g, 75%); distilled under reduced pressure (1 mmHg, b.p. 85–90 °C); δ_H(80 MHz; $CDCl_3$) 4.64 (2 H, s, CH_2CO), 2.18 and 2.14 (6 H, 2s, *Me*$COCH_2$ and *Me*CO–CMe_2) and 1.50 (6 H, s, Me_2C); ν/cm^{-1} 1752 and 1733 (C=O).

1,1-*Dimethyl*-2-*oxopropyl* 1-*methylprop*-2-*ynyl carbonate* **3g**. Method B colourless liquid (1.80 g, 90%); distilled under reduced pressure (0.7 mmHg, b.p. 55–60 °C); δ_H(300 MHz; $CDCl_3$) 5.26 (1 H, q, ^3J 6.7, Me*CH*), 2.55 (1 H, s, ≡CH), 2.18 (3 H, s, MeCO), 1.57 (3 H, d, ^3J 6.7, CH*Me*) and 1.55 (6 H, s, Me_2C); ν/cm^{-1} 3290 (≡CH), 1746 and 1725 (C=O).

1,1-*Dimethylprop*-2-*ynyl* 1-*ethyl*-1-*methyl*-2-*oxopropyl carbonate* **3h**. Method B white solid (1.69 g, 75%); recrystallized from ether and hexane; m.p. 54–56 °C; δ_H(300 MHz; $CDCl_3$) 2.52 (1 H, s, ≡CH), 2.12 (3 H, s, MeCO), 1.71 and 1.90 (2 H, 2 dq, ^2J 15.0 and ^3J 7.5, CH_2Me), 1.67 (6 H, s, Me_2C) and 0.86 (3 H, t, ^3J 7.5, *Me*CH_2); ν/cm^{-1} 3270 (≡CH), 1742 and 1721 (C=O) (Found: C, 63.95; H, 8.03. $C_{12}H_{18}O_4$ requires C, 63.68; H, 8.02%).

1,1-*Dimethyl*-2-*oxopropyl* 1-*butyl*-1-*methylprop*-2-*ynyl carbonate* **3i**. Method B colourless liquid (1.55 g, 62%); distilled under reduced pressure (0.5 mmHg, b.p. 90 °C); δ_H(300 MHz; $CDCl_3$) 2.52 (1 H, s, ≡CH), 2.11 (3 H, s, MeCO), 1.96–1.77 (2 H, m, CH_2CO), 1.63 (3 H, s, *Me*CCH_2), 1.44 (6 H, s, Me_2C), 1.48–1.32 (2 H, m, $CH_2CH_2CH_2$), 1.29 (2 H, sext, ^3J 7.3, CH_2Me) and 0.86 (3 H, t, ^3J 7.2, *Me*CH_2); ν/cm^{-1} 3286 (≡CH) 1749 and 1725 (C=O).

4-*Methoxy*-4,5,5-*trimethyl*-1,3-*dioxolan*-2-*one* **4** from **2a**. Method B white solid (0.75 g, 47%); distilled under reduced pressure (0.5 mmHg, b.p. 40 °C); δ_H(300 MHz; $CDCl_3$) 3.40 (3 H, s, MeO), 1.49 (3 H, s, MeC), 1.40 and 1.38 (6 H, 2s, Me_2C); ν/cm^{-1} 1797 (C=O) (Found: C, 52.48; H, 7.52. $C_7H_{12}O_4$ requires C, 52.49; H, 7.55%).

Acknowledgements

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