An Efficient and Selective Palladium-catalysed Oxidative Dicarbonylation of Alkynes to Alkyl- or Aryl-maleic Esters

Bartolo Gabriele,[a] Mirco Costa,[b] Giuseppe Salerno[a] and Gian Paolo Chiusoli[b]
[a] *Dipartimento di Chimica, Università della Calabria, I-87030 Arcavacata di Rende, Cosenza, Italy*
[b] *Dipartimento di Chimica Organica e Industriale dell'Università, Viale delle Scienze, I-43100 Parma, Italy*

Terminal alkyne dicarbonylation can be readily effected under mild conditions by treating alkynes with carbon monoxide and alcohols or water at 25–80 °C in the presence of PdI_2, KI and air, with unprecedented catalytic efficiency. Dicarbonylated products are mainly maleic esters or acids and their ring-chain tautomers. The latter are formed to a large extent at room temperature. Reaction pathways are discussed.

Dicarbonylation of alkynes with carbon monoxide has been known for several years,[1] but even the most recent literature reports methods which are not completely satisfactory[2] particularly from the standpoint of catalytic efficiency. However, alkyl- or aryl-maleic esters and acids are interesting products, which can be used as monomers for polymerization,[3] so an efficient procedure to prepare these compounds is a useful target. We now report such a procedure, which affords high yields of alkyl- or aryl-maleic esters and acids under mild conditions. A preliminary account, limited to prop-2-ynyl alcohol, was published recently.[4]

Results and Discussion

Our method consists of the reaction of alkynes RC≡CH in alcohols or water-containing solvents at 25–80 °C under a moderate pressure of carbon monoxide (15–25 atm) and air (6–10 atm) in the presence of PdI_2 and excess of KI (10 mol, corresponding to K_2PdI_4 + 8KI) [eqn. (1)].

$$RC{\equiv}CH + 2CO + 2R'OH + \tfrac{1}{2}O_2 \xrightarrow{\text{Pd cat.}} RC(CO_2R')=CH(CO_2R') + H_2O \quad (1)$$

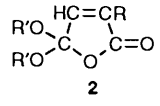
Table 1 reports the results obtained with different alkynes, namely HC≡CH, BuC≡CH, PhC≡CH, $HC{\equiv}CCH_2OH$ and $HC{\equiv}CCH_2OAc$. The products obtained (**1–7**) are mainly dicarbonylated compounds (**1–6**), predominantly in the *Z* form, as expected in view of the *cis* character of the carbon monoxide insertion reaction.[5] The presence of a small amount of the *E* form is to be ascribed to an isomerization process at some stage of the catalytic process.

Within the *Z* series two other types of compounds are present, beside the maleic esters: ring-chain tautomers **2** and acids **3**. Formation of the latter is due to the presence of water in the reaction mixture. The *E*-compounds consist of the fumaric esters **4**. Traces of lactone **8** are formed in the case of prop-2-ynyl alcohol. When a hydroxy or acetoxy group is present a side reaction is the etherification to **5**. The *E*-stereochemistry was assigned to this compound on the basis of the similar chemical shifts of the =CH proton of substituted fumaric esters, which are at a remarkably lower field than the corresponding maleic esters [see also ref. 2(*a*)]. Finally, a small amount of product **7**, deriving from methoxy–methoxycarbonylation, is present in the reaction of hex-1-yne. The *Z* stereochemistry was attributed to this compound because of the absence of a coupling constant of the order of 0.4 Hz between the methyl and vinyl protons observed for analogous *E* compounds.[6]

Table 1 lists a series of experiments carried out with differently substituted terminal alkynes in methanol as solvent.

$(R'O_2C)HC{=}CR(CO_2R')$ *Z* **1**

a R = H, R' = Me
b R = Bu, R' = Me
c R = Ph, R' = Me
d R = CH_2OH, R' = Me
e R = CH_2OAc, R' = Me
f R = Bu, R' = Bu



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a R = Bu, R' = Me
b R = Ph, R' = Me
c R = CH_2OH, R' = Me
d R = CH_2OAc, R' = Me
e R = Bu, R' = Bu

$(HO_2C)HC{=}CR(CO_2H)$ *Z* **3**

a R = Bu
b R = Ph

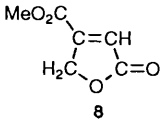
$(R'O_2C)HC{=}CR(CO_2R')$ *E* **4**

a R = H, R' = Me
b R = Bu, R' = Me
c R = Ph, R' = Me
d R = Bu, R' = Bu

$(MeO_2C)HC{=}C(CO_2Me)CH_2OMe$ *E* **5**

$(MeO_2C)HC{=}C(OMe)Bu$ *Z* **7**

$(MeO_2C)HC{=}CHCH{=}CH(CO_2Me)$ *Z Z* **6**



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These experiments were aimed at achieving efficiency (number of molecules of dicarbonylated products per molecule of catalyst) and selectivity (number of molecules of dicarbonylated products in respect to the total formed) at high conversion. For each substrate the concentration was kept constant and the substrate to catalyst ratio was varied. When high conversions were attained, however, yields and total selectivity in dicarbonylated products were similar to those obtained if the catalyst concentration was kept constant and the substrate to catalyst ratio varied, as shown by comparison of run 4 with run 3.

Different substrate concentrations were used for different substrates either to decrease reaction time (hex-1-yne required a higher concentration than phenylacetylene) or to improve selectivity (prop-2-ynyl alcohol and its acetate required a lower concentration to minimize the formation of compounds **5** and **8**).

Inspection of Table 1 shows that on passing from 25 to 80 °C catalytic efficiency increases and reaction time decreases, while total yield decreases to some extent. The most abundant by-product is compound **2**, which reaches the highest value (45%) with phenylacetylene at 25 °C. At higher temperature and/or for

Table 1 Reactions of alkynes RC≡CH with CO–air, 3:1 and MeOH, initial pressure 20 atm at 20 °C, PdI_2–KI molar ratio 1:10, alkyne conc./mol dm^{-3} (in MeOH)[a]: 0.13 (HC≡CH), 0.70 (BuC≡CH), 0.50 (PhC≡CH), 0.26 ($HOCH_2C$≡CH) or ($AcOCH_2C$≡CH)

Run	R (mmol)	mol substrate / mol catalyst	T/°C	t/h	Conv. (%)[b]	Yields (%)[b] 1	2	3	4	5	6	7	Total yield (%)[c]	mol prod. / mol cat.
1	H (33)	1450	60	15	99	89			3		7		99	1435
2	Bu (14)	300	40	15	100	65	20	5	8			2	98	300
3	Bu (14)	500	60	3	92	65	13	5	7			2	90	460
4	Bu (23)	500	60	3	92	62	13	5	10			2	90	460
5	Bu (14)	1000	60	6	96	67	13	8	6			2	94	960
6	Bu (25)	3000	60	48	75	53		14	5			3	72	2250
7	Bu (25)	3000	80	15	72	53		9	6			1	68	2070
8	Ph (14)	200	25	15	96	36	45	6	9				96	192
9	Ph (14)	500	40	15	100	42	44	5	9				100	500
10	Ph (14)	1000	60	3	96	46	37	5	8				96	960
11	Ph (25)	3000	60	15	94	46	21	14	6				87	2610
12	Ph (25)	3000	80	15	80	45	10	13	5				73	2190
13	CH_2OH (28)	3000	25	15	96	72	23			1			96	2880
14	CH_2OH (28)	4000	40	15	93	77	13			3			93	3720
15	CH_2OH (28)	5000	60	15	97	63				17			80	4000
16	CH_2OH (28)	5000	80	15	96	42				26			68	3400
17	CH_2OAc (10)	1000	25	5	98	52	44			2			98	980
18	CH_2OAc (14)	2000	40	3	96	56	37			3			96	1920
19	CH_2OAc (40)	4000	40	15	100	56	34			9			99	3960

[a] Alkyne concentration is constant while Pd concentration varies for each substrate as indicated above except for run 4, where Pd concentration is the same as in run 2 but the alkyne concentration is varied (1.17 mol dm^{-3} MeOH). [b] Based on starting alkyne, by GLC. [c] Dicarbonylated compounds only.

longer time it converts into its tautomer **1** (main product). The latter can also be obtained quantitatively by acid-catalysed alcoholysis of **2**. Under the same conditions as reported in Table 1 for terminal alkynes the internal ones react to a very limited extent.

It is worth noting that the carbonylation process is selective towards the triple bond, the hydroxy function not undergoing carbonylation. The process described here is also characterized by an unusual catalytic efficiency. For example, in the case of prop-2-ynyl alcohol up to 4000 mol of substrate per mol of catalyst have been transformed (run 15) without optimization work.

The study of the effect of catalyst composition has shown that $PdCl_2$ + 10 KCl is hardly reactive with hex-1-yne, while $PdBr_2$ + 10 KBr gives only an 8% conversion under the same conditions leading to 92% with PdI_2 + 10 KI. The excess KI plays an important role insofar as it stabilizes the PdI_4^{2-} anion. No KI excess adversely affects selectivity while a large excess (> 50 mol per mol of Pd) greatly depresses the reaction rate. Although not completely optimized, an excess of 8 mol KI, with respect to PdI_4^{2-}, turns out to be an appropriate compromise.

The reaction was successfully extended to other alochols such as the butyl one. Under conditions similar to those of run 3 the reaction of hex-1-yne in butanol, containing 30% of dimethylacetamide (to favour PdI_2 dissolution), required a longer reaction time, giving *ca.* 90% conversion in 15 h at 60 °C, with 55% yield of **1f**, 14% of **2e** and 11% of **4d** (400 mol of dicarbonylated products per mol of Pd).

Another aspect worth mentioning is that it is also possible to work in water as the reaction medium, using a homogenizing solvent such as dimethylacetamide. Under the same conditions as run 10, but using a 10% solution of water in dimethylacetamide in place of methanol, the reaction proceeded much more slowly. After 24 h at 60 °C conversion was 40% while selectivity (phenylmaleic and phenylfumaric acids, 9:1) reached 75%.

Although kinetics are not reported here the mechanism appears straightforward in its essential lines in view of existing knowledge.[7,8] The reaction is initiated by the alkoxy- or hydroxy-carbonyl group which is formed on palladium[8] and then transferred to the alkyne (Scheme 1).

A similar pathway except for the first CO insertion step explains the alkoxy–alkoxycarbonylation to **7**. The *Z*-stereochemistry implies that the stereochemistry of methoxy and methoxycarbonyl addition to the triple bond is *cis*. Alkoxy–alkoxycarbonylation of alkynes thus appears to conform to the general rule of *cis* insertion of carbon monoxide.[5,7]

A second molecule of the alkyne is inserted before the second molecule of CO in the case of acetylene [formation of dialkyl (*Z*,*Z*)-muconate].

As mentioned above, $PdCl_2$ and $PdBr_2$ are not effective as catalysts. This is due to the difficulty of reoxidizing palladium(0) or an H–Pd–X intermediate (X = halide) to palladium(II) with O_2–HCl or O_2–HBr. In contrast, palladium(0) (or an H–Pd–I complex) is readily oxidized to palladium iodide. We could ascertain that the process is so effective that even a palladium sponge can be solubilized by the reaction of HI + KI + O_2 or I_2 + KI. The recently proposed intermediacy of a palladium hydroperoxide[2b,9] is probably not needed in our case.

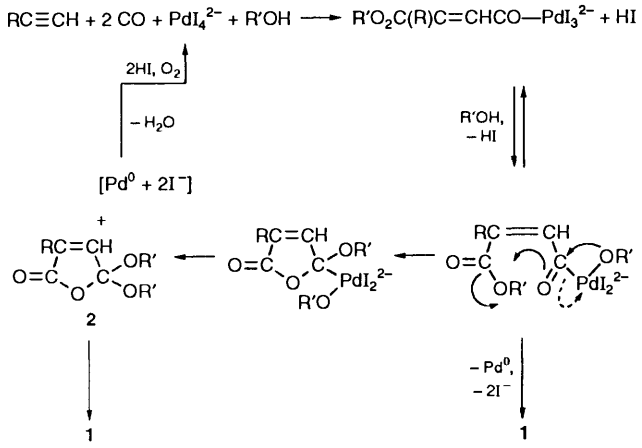
The products resulting from ring–chain tautomerism (R′ = alkyl) are probably formed according to Scheme 2, and are readily transformed into the *Z* isomers of **1**. Palladium alkoxides, which under the reaction conditions must be present in the mixture,[8] are likely to catalyse ring formation analogously

$$R'OH + PdI_4^{2-} \rightleftharpoons R'O\text{–}PdI_3^{2-} + HI \xrightarrow{CO} R'O_2C\text{–}PdI_3^{2-} \xrightarrow{RC\equiv CH}$$

$$\longrightarrow R'O_2C(R)C{=}CH\text{–}PdI_3^{2-} \xrightarrow{CO} R'O_2C(R)C{=}CHCO\text{–}PdI_3^{2-} \xrightarrow{R'OH}$$

$$\longrightarrow R'O_2C(R)C{=}CHCO_2R' + [Pd^0 + HI + 2I^-] \xrightarrow{HI,\,O_2} PdI_4^{2-} + H_2O$$

Scheme 1



Scheme 2

to other alkoxides which catalyse ring–chain tautomerizations.[10] The alkoxy group then cleaves the palladium–carbon bond to form **2**. The latter is readily transformed into the *Z*-isomer **1**, particularly at temperatures higher than 40 °C. Compound **1** can also be formed directly from the intermediate acyl(alkoxy)diiodopalladate (dashed arrow). R'OH attack on the palladium-bonded carbonyl rather than on palladium itself is another possibility, however. As mentioned above, in the presence of oxygen and HI a fast reoxidation of palladium(0) to palladium(II) takes place.

In the presence of water (R' = H) the process would lead to the corresponding substituted maleic anhydrides as intermediates in the formation of the acids actually isolated in our procedure.

Scheme 2 also provides an explanation for the recent finding by Zargarian and Alper[2b] who found that, at room temperature, dicarbonylation of alkynes in the presence of formic acid, $PdCl_2$ and $CuCl_2$ gave substituted maleic anhydrides.

The presence of a significant amount of the allylic methyl ether **5** in the reactions of prop-2-ynyl alcohol and of prop-2-ynyl acetate can be interpreted as occurring *via* an allylic complex of palladium formed from **1d** or **1e**, which causes *syn* to *anti* conversion and is then attacked by methanol on the methylene group to give the *E* isomer **5**. Accordingly, compound **1d** is converted into **5** under the reaction conditions, while in the absence of palladium it remains unchanged. Analogously to methoxycarbonylation, methoxylation of an allylpalladium complex must liberate palladium(0), which, however, would become available again for oxidation by iodine according to Schemes 1 and 2.

Catalyst deactivation seems to occur significantly at temperatures higher than 60 °C.

In conclusion, the oxidative dicarbonylation can be carried out with high selectivity and efficiency in the presence of a catalytic system based on the PdI_4^{2-} anion under conditions allowing continuous reoxidation of palladium(0).

Experimental

All starting acetylenic substrates were commercial products (Aldrich, Fluka, Strem), except prop-2-ynyl acetate which was prepared by acetylation of prop-2-ynyl alcohol and was used after distillation.

Product mixtures were analysed by TLC or by GLC using capillary columns with dimethylpolysiloxane (HP-1) or TPA modified polyethyleneglycol (HP-FFAP) as the stationary phase. Quantitative determination of the products, if not otherwise specified, was carried out by using the internal standard method.

Products were separated by conventional extraction techniques, followed by distillation and/or by chromatographic procedures on silica gel with suitable eluents. Merck silica gel 60 (60–230 mesh) was used for column chromatography. Analytical TLC plates and silica gel 60F254 for PLC were purchased from Merck. Elemental analyses were carried out with a Carlo Erba Elemental Analyser Mod. 1106. IR spectra were recorded on a Perkin-Elmer System 2000 FTIR spectrometer. Mass spectra were obtained using a VG Trio-2 spectrometer at 70 eV ionizing voltage. ^1H NMR spectra were taken on AC300 or AMX400 Bruker spectrometers and are reported in δ units with Me_4Si as internal standard; *J* values are given in Hz.

Catalytic Oxidative Carbonylation.—The carbonylation reactions were carried out in a Brignole or Parr stainless-steel autoclave with magnetic stirring. The substrate to catalyst ratios are indicated in Table 1. Care must be taken to fill the autoclave to levels that allow the presence of a sufficient amount of oxygen necessary for the reoxidation cycle.

Catalytic Oxidative Dicarbonylation of Acetylene.—In a 500 cm^3 Hastelloy autoclave (Brignole) PdI_2 (8.3 mg, 0.023 mmol), KI (35.5 mg, 0.214 mmol) and methanol (250 cm^3) were charged in the presence of air. Acetylene (0.86 g, 33.08 mmol) was slowly dissolved into the reaction mixture at 0 °C. Carbon monoxide (25 atm) and air (up to 34 atm of total pressure) were then introduced and the mixture was stirred at 60 °C for 15 h. Acetylene was converted completely. After filtration of the reaction mixture, the products, dimethyl fumarate (0.153 g, 3%), dimethyl maleate (4.224 g, 89%) and (*Z*,*Z*-dimethyl muconate (0.291 g, 7%) were identified by comparison with authentic samples (GLC and mass spectroscopy).

General Procedure for Catalytic Carbonylation of Acetylenic Substrates.—In a typical experiment a 600 cm^3 stainless-steel autoclave (Parr) was charged in the presence of air with PdI_2, KI and the appropriate acetylenic derivative dissolved in MeOH in the molar ratio reported in Table 1. The autoclave was pressurized with CO (15 atm) and air (up to 20 atm of total pressure) and heated and stirred at the temperature and for the time required to obtain a satisfactory conversion (Table 1). After filtration the carbonylated products were separated by chromatographic procedures as reported below. The total yields by weight were in accord with GLC yields.

Separation of Products.—Compounds **7**, **4b**, **2a**, **1b** and **3a**, deriving from the reaction of BuC≡CH, were eluted in this order by chromatography through a SiO_2 column, using as eluent a mixture of hexane–ethyl acetate in decreasing ratio from 99:1 to 0:100. Compound **1f** was separated in a similar way from **2e** and **4d**. Compounds **2b**, **4c**, **1c** and **3b** were also eluted in a concentration gradient as above, the last one (m.p. 104–105 °C) with pure ethyl acetate.[11] Compound **1d** from prop-2-ynyl alcohol was obtained by distillation (110 °C/0.18 mmHg) of a CH_2Cl_2 extract of the residue obtained by removing the solvent from the crude reaction product. Using column chromatography on SiO_2 with hexane–ethyl acetate 1:1 as eluent compounds **1d** and **2c** were obtained as a mixture, which was further separated by preparative GLC (SE30 packed column). The *E*-derivative corresponding to **1d** was found to be present in traces as lactone **8**. Pure compound **8** was obtained from an experiment similar to run 14 but with a higher substrate concentration (0.5 mol dm^{-3}). Chromatographic separation was effected on the crude reaction mixture first on a SiO_2 column (hexane–ethyl acetate, 1:1), then on a preparative SiO_2 plate using the same eluent. Compound **5** was obtained in a pure state from the reaction of prop-2-ynyl acetate, by

distillation (60 °C/0.1 mmHg) of a CH_2Cl_2 extract obtained as above, neutralized by the addition of aq. $NaHCO_3$, extracted with CH_2Cl_2 and dried with $CaCl_2$. The following fraction (68–70 °C/0.05 mmHg) contained a mixture of compounds **1e** and **2d**. This fraction was separated by TLC (hexane–ethyl acetate, 7:3) to obtain pure **1e**, while **2d** was isolated by preparative GC.

Identification of known compounds was carried out by comparison with commercial samples (**1a**, **4a**) or with literature data (**1b**, **3a**, **4b**, **4d**),[12] (**1c**, **3b**)[13] and (**4c**).[14] New compounds were identified by chemical and spectroscopic methods. Compounds **2a–e** were converted into the corresponding maleates by acid hydrolysis in methanol or butanol. For example, compound **2a** (50 mg) was dissolved in MeOH (3 cm^3) and two drops of conc. H_2SO_4 were added to the mixture which was refluxed for 5 h. GC Analysis showed that the corresponding dimethyl maleate derivative was formed quantitatively. Compound **1d** was reported in our preliminary paper which also described its transformation into aconitic esters.[4] Under the same conditions compounds **1e** and **5** underwent the same transformation. Compound **7** was compared with an original sample prepared synthetically[15] and its stereochemistry assigned on the basis of ^1H NMR data.

Characterization of Products.—*Dimethyl* (Z)-2-*hydroxymethylbut*-2-*enedioate* **1d**. Colourless oil (Found: C, 48.3; H, 5.7. $C_7H_{10}O_5$ requires C, 48.28; H, 5.75%); ν_{max}(film)/cm^{-1} 3492s, br, 3006w, 2956m, sharp, 1725–1740s, 1658m, 1438s, 1380m, 1332s, 1275s, 1204s, 1172s, 1055m, 1019m and 987w; δ_H(300 MHz; $CDCl_3$) 3.68 (3 H, s, CO_2Me), 3.75 (3 H, s, CO_2Me), 4.30 (2 H, d, *J* 1.97, CH_2) and 6.13 (1 H, t, *J* 1.97, =CH); *m/z* 174 (M^+, absent), 159 (6), 145 (18), 143 (75), 142 (60), 115 (34), 114 (15), 113 (100), 111 (12), 110 (72), 85 (11), 83 (66), 82 (12), 59 (53), 55 (54) and 53 (24).

Dimethyl (Z)-2-*acetoxymethylbut*-2-*enedioate* **1e**. Colourless oil (Found: C, 50.05; H, 5.5. $C_9H_{12}O_6$ requires C, 50.00; H, 5.56%); ν_{max}(film)/cm^{-1} 2957m, 1725–1750s, 1661m, 1438s, 1371s, 1338m, 1262s, 1220s, 1173s, 1050m, 1029m and 878w; δ_H(300 MHz, $CDCl_3$) 2.12 (3 H, s, Me), 3.77 (3 H, s, CO_2Me), 3.84 (3 H, s, CO_2Me), 4.82 (2 H, d, *J* 1.70, CH_2) and 6.19 (1 H, t, *J* 1.70, =CH); *m/z* 216 (M^+, absent), 185 (2), 157 (52), 143 (100), 141 (94), 140 (16), 115 (88), 113 (21), 110 (62), 83 (16), 59 (18) and 53 (11).

Dibutyl (Z)-2-*butylbut*-2-*enedioate* **1f**. Colourless oil (Found: C, 67.6; H, 9.8. $C_{16}H_{28}O_4$ requires C, 67.61; H, 9.86%); ν_{max}(film)/cm^{-1} 2980s, 2945s, 2900s, 1720–1740s, 1650m, 1460m, 1400m, 1370m, 1320m, 1260s, 1215w, 1180s, 1090m, 1020m, 980w, 870w and 740m; δ_H(300 MHz, $CDCl_3$) 0.93 (3 H, t, *J* 7.2, Me), 0.95 (3 H, t, *J* 7.4, Me), 0.97 (3 H, t, *J* 7.4, Me), 1.34–1.52 (8 H, m system, 4 × CH_2), 1.60–1.73 (4 H, 2 × m, 2 × CH_2), 2.37 (2 H, dt, *J* 1.5, 7.6, =CCH_2), 4.13 (2 H, t, *J* 6.7, OCH_2), 4.25 (2 H, t, *J* 6.7, OCH_2) and 5.81 (1 H, t, *J* 1.5, =CH); *m/z* 284 (M^+, absent), 229 (54), 227 (26), 211 (46), 155 (100), 126 (31), 113 (70), 112 (79), 81 (80), 57 (78), 56 (30) and 55 (20).

3-*Butyl*-5,5-*dimethoxyfuran*-2(5H)-*one* **2a**. Colourless oil (Found: C, 60.1; H, 8.0. $C_{10}H_{16}O_4$ requires C, 60.00; H, 8.00%); ν_{max}(film)/cm^{-1} 2957s, 2874m, 1780s, 1667s, 1466m, 1443m, 1309s, 1201m, 1141s, 1121s, 1081m, 1030m, 1003s, 948s, 873m, 783w, 755w, 736w, 679w and 660w; δ_H(300 MHz, $CDCl_3$) 0.94 (3 H, t, *J* 7.3, Me), 1.38 (2 H, sext, *J* 7.4, CH_2), 1.56 (2 H, quint, *J* 7.4, CH_2), 2.32 (2 H, td, *J* 7.4, 1.5, CH_2), 3.43 (6 H, s, 2 × OMe) and 6.60 (1 H, t, *J* 1.5, =CH); *m/z* 200 (M^+, absent), 169 (100), 141 (9), 127 (24), 113 (11), 99 (86), 81 (37), 79 (9), 74 (8), 68 (12), 67 (14), 59 (30), 55 (27) and 53 (14).

5,5-*Dimethoxyfuran*-3-*phenyl*-2(5H)-*one* **2b**. Colourless oil (Found: C, 65.5; H, 5.4. $C_{12}H_{12}O_4$ requires C, 65.45; H, 5.45%); ν_{max}(film)/cm^{-1} 3088w, 2951m, 2845w, 1773s, 1642w, 1494m, 1450m, 1317s, 1278m, 1232m, 1190m, 1139m, 1066m, 1002m, 948m, 923m, 857w, 794m, 742m and 693m; δ_H(300 MHz, $CDCl_3$), 3.50 (6 H, s, 2 × OMe), 7.10 (1 H, s, =CH), 7.42–7.45 (3 H, m, 2 m + 1 p aromatic H) and 7.84–7.87 (2 H, m, 2 *o* aromatic H); *m/z* 220 (M^+, 13), 192 (49), 189 (63), 161 (93), 144 (13), 131 (49), 118 (33), 117 (55), 116 (21), 115 (53), 105 (15), 103 (46), 102 (100), 99 (33), 91 (32), 77 (15), 76 (24), 75 (22), 74 (13), 71 (11), 69 (11) and 59 (30).

3-*Hydroxymethyl*-5,5-*dimethoxyfuran*-2(5H)-*one* **2c**. Colourless oil (Found: C, 48.3; H, 5.7. $C_7H_{10}O_5$ requires C, 48.28; H, 5.75%); ν_{max}(film)/cm^{-1} 3490s, br, 2960m, 1775s, 1655m, 1335s, 1305s, 1115m, 1015m, 943m, 873m and 762w; δ_H(300 MHz, $CDCl_3$) 3.38 (6 H, s, 2 × OMe), 4.36 (2 H, d, *J* 2.0, CH_2) and 6.90 (1 H, t, *J* 2.0, =CH); *m/z* 174 (M^+, absent), 143 (67), 142 (10), 115 (39), 113 (23), 110 (16), 99 (100), 87 (11), 85 (25), 84 (12), 83 (78), 71 (10), 69 (11), 68 (11), 59 (65), 55 (94) and 53 (35).

3-*Acetoxymethyl*-5,5-*dimethoxyfuran*-2(5H)-*one* **2d**. Colourless oil (Found: C, 50.0; H, 5.6. $C_9H_{12}O_6$ requires C, 50.00; H, 5.56%); ν_{max}(film)/cm^{-1} 3097w, 2956m, 1780s, 1307s, 1143s, 1087m, 999m, 949m, 872m, 783w and 754w; δ_H(300 MHz, $CDCl_3$), 2.14 (3 H, s, Me), 3.45 (6 H, s, 2 × OMe), 4.86 (2 H, d, *J* 1.74, CH_2) and 6.92 (1 H, t, *J* 1.74, =CH); *m/z* 216 (M^+, absent), 185 (9), 143 (100), 130 (50), 115 (65), 113 (49), 99 (8), 85 (33), 83 (19), 69 (12), 68 (13), 59 (23), 55 (13) and 53 (12).

5,5-*Dibutoxy*-3-*butylfuran*-2(5H)-*one* **2e**. Colourless oil (Found: C, 67.6; H, 9.8. $C_{16}H_{28}O_4$ requires C, 67.61; H, 9.86%); ν_{max}(film)/cm^{-1} 2960s, 2930s, 2870s, 1780s, 1460m, 1435m, 1295s, 1135s, 1110m, 1030m, 1000s, 950s, 880w, 780w and 750w; δ_H(400 MHz, $CDCl_3$), 0.94 (3 H, t, *J* 7.2, Me), 0.95 (3 H, t, *J* 7.4, Me), 0.97 (3 H, t, *J* 7.4, Me), 1.32–1.34 (8 H, m system, 4 × CH_2), 1.61–1.73 (4 H, 2 × m, 2 × CH_2), 2.33 (2 H, td, *J* 7.6, 1.6, CH_2), 3.42 (2 H, t, *J* 6.7, OCH_2), 3.45 (2 H, t, *J* 6.6, OCH_2) and 6.61 (1 H, t, *J* 1.6, =CH); *m/z* 284 (M^+, absent), 256 (8), 199 (14), 183 (22), 159 (16), 145 (28), 127 (71), 115 (22), 103 (63), 102 (51), 99 (23), 87 (24), 85 (47), 84 (30), 69 (29), 57 (100), 56 (73) and 55 (44).

Dimethyl (E)-2-*methoxymethylbut*-2-*enedioate* **5**. Colourless oil (Found: C, 51.1; H, 6.35. $C_8H_{12}O_5$ requires C, 51.06; H, 6.38%); ν_{max}(film)/cm^{-1} 2995m, 2955m, 2824w, 1725–1750s, 1654m, 1437s, 1350m, 1286s, 1215s, 1117s, 1030m, 1002m, 960m, 911m, 840w and 787m; δ_H(300 MHz, $CDCl_3$), 3.37 (3 H, s, OMe), 3.80 (3 H, s, CO_2Me), 3.84 (3 H, s, CO_2Me), 4.58 (2 H, d, *J* 0.73, CH_2) and 6.85 (1 H, t, *J* 0.73, =CH); *m/z* 188 (M^+, absent), 157 (54), 156 (100), 140 (21), 129 (11), 128 (13), 126 (10), 113 (58), 100 (22), 98 (32), 97 (41), 84 (13), 75 (31), 69 (45), 59 (32) and 53 (12).

Methyl (Z)-3-*methoxyhept*-2-*enoate* **7**. Colourless oil (Found: C, 62.7; H, 9.3. $C_9H_{16}O_3$ requires C, 62.79; H, 9.30%); ν_{max}(film)/cm^{-1} 2963m, 2860w, 1720s, 1626s, 1436m, 1413m, 1379m, 1262m, 1192m, 1143s, 1110m, 1054m, 820m; δ_H(300 MHz, $CDCl_3$), 0.91 (3 H, t, *J* 7.25, Me), 1.36 (2 H, sext, CH_2), 1.53 (2 H, quint, CH_2), 2.74 (2 H, t, *J* 7.6, CH_2), 3.62 (3 H, s, OMe), 3.67 (3 H, s, CO_2Me), 4.98 (1 H, s, =CH); *m/z* 172 (M^+, 23), 144 (31), 141 (54), 130 (100), 115 (13), 111 (98), 102 (30), 101 (28), 99 (33), 98 (13), 85 (13), 83 (16), 81 (20), 79 (12), 73 (11), 72 (47), 71 (13), 69 (33), 68 (13), 59 (40), 55 (18) and 53 (11).

Methyl 2,5-*dihydro*-5-*oxofuran*-3-*carboxylate* **8**. Colourless oil (Found: C, 50.75; H, 4.15. $C_6H_6O_4$ requires C, 50.70; H, 4.23%); ν_{max}(film)/cm^{-1} 3056m, 2957w, 1783s, 1736s, 1439m, 1311w, 1266s, 1148m, 1032m, 894m and 738s; δ_H(300 MHz, $CDCl_3$) 3.87 (3 H, s, CO_2Me), 5.00 (2 H, d, *J* 2.25, CH_2) and 6.70 (1 H, t, *J* 2.25, =CH); *m/z* 142 (M^+, 17), 114 (18), 113 (100), 111 (51), 110 (44), 85 (16), 83 (24), 82 (20), 81 (13), 74 (10), 59 (26), 55 (27) and 53 (53).

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