Synthesis of Maleic Anhydrides and Maleic Acids by Pd-Catalyzed Oxidative Dicarbonylation of Alk-1-ynes

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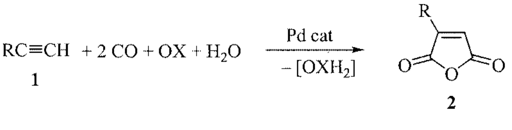
We have found that carbon dioxide effectively promotes the Pd-catalyzed oxidative carbonylation of terminal alkynes to give maleic anhydrides in fair yields. Reactions were carried out in aqueous dioxane at 60–80 °C in the presence of catalytic amounts of PdI_2 in conjunction with KI and under a 4:1:10 mixture of $CO/air/CO_2$ (60 atm total pressure at 25 °C). By working in the presence of a large excess of water, maleic acids were formed selectively with unprecedented catalytic efficiencies for this kind of reaction. In the latter case, the use of an excess of carbon dioxide tended to inhibit, rather than promote, the reaction.

Introduction

Maleic anhydrides and acids are important classes of carbonyl compounds. Maleic anhydrides are useful intermediates in organic synthesis,[1−3] and have found application both in the preparation of biologically active molecules[4] and as monomers for polymerization.[5] Maleic acids are mainly employed as starting materials for polymerization reactions,[6] and have also found application as synthetic intermediates.[7]

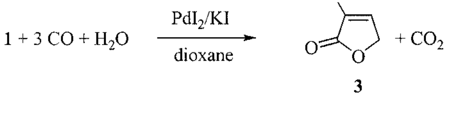
Pd-catalyzed oxidative carbonylation of alk-1-ynes **1** in the presence of small amounts of water represents a valuable method for the direct synthesis of maleic anhydrides **2** starting from readily available substrates [Equation (1)].[8]



(1)

The stoichiometric formation of phenylmaleic anhydride by carbonylation of phenylacetylene in the presence of $PdCl_2$ and $HgCl_2$ in acetone/H_2O (9:1, v/v) at room temp. and under a pressure of 2 atm of CO was reported many years ago.[9] In a later report, maleic anhydrides were obtained with good selectivities and under mild conditions by the oxidative carbonylation of alk-1-ynes in $THF/HCO_2H/H_2O$ in the presence of $PdCl_2$ as catalyst, $CuCl_2$ as cocatalyst, and O_2 as reoxidant {Equation (1), [OX] = 1/2 O_2, [OXH_2] = H_2O}.[10] More recently, the use of $PdCl_2$ as the catalyst and $CuCl_2$ as the oxidizing agent in water/dioxane has been described {Equation (1), [OX] = 2 $CuCl_2$, OXH_2 = 2 CuCl + 2 HCl}.[11] Halide-free catalytic systems have also been reported, both homogeneous [$Pd(OAc)_2$ in conjunction with chlorohydroquinone (HQ-Cl), molybdovanadophosphate (NPMoV) and CH_3SO_3H][12] and heterogeneous [Pd^{II}/zirconium phosphate].[13]

In the framework of our investigations on the carbonylation of alkynes, we have previously studied the PdI_2/KI-catalyzed carbonylation of **1** carried out in dioxane under *reductive* conditions (CO/H_2O in the absence of O_2), which led selectively to 3-substituted furan-2(5*H*)-ones **3** in the absence of CO_2 [Equation (2)][14] and to a ca. 1:1 mixture of **3** and **2** in the presence of CO_2 (40 atm) [Equation (3)].[15−16]



(2)

$$2\,\mathbf{1} + 4\,CO + H_2O \xrightarrow[\text{dioxane}]{PdI_2/KI \quad CO_2} \mathbf{2} + \mathbf{3} \qquad (3)$$

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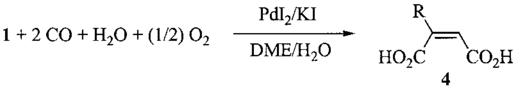
We now report the selective synthesis of **2** by Pd-catalyzed and CO_2-promoted oxidative carbonylation of **1**, based on the use of a very simple catalytic system (PdI_2 + 10 equiv. of KI), in water/dioxane as the solvent and with oxygen as the oxidizing agent [Equation (4)]. This catalytic system has also proved useful — with unprecedented catalytic efficiencies for this kind of reaction — for the preparation of maleic acids **4** from **1** by working in 1,2-dimethoxyethane (DME) with water as the cosolvent [Equation (5)]. In the latter case, the use of an excess of carbon dioxide tends to inhibit, rather than promote, the reaction.

$$\mathbf{1} + 2\,CO + (1/2)\,O_2 \xrightarrow[\text{H}_2\text{O, CO}_2 \text{ dioxane}]{\text{PdI}_2\text{/KI}} \mathbf{2} \qquad (4)$$



(5)

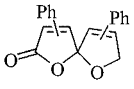
Results and Discussion

Synthesis of Maleic Anhydrides 2

Oxidative carbonylation reactions of alk-1-ynes **1** were carried out in dioxane at 60−80 °C in the presence of PdI_2 (5×10^{-3} to 1×10^{-2} equiv.), KI (0.05−0.10 equiv.), and H_2O (2.0−2.5 equiv.) under a 4:1:10 mixture of CO/air/CO_2 (60 atm total pressure at 25 °C) and afforded maleic anhydrides **2** in fair to excellent yields [48−96%, Equation (4)]. Representative results obtained with different alk-1-ynes **1** are shown in Table 1.

Arylacetylenes were sufficiently reactive to allow the reaction to be conducted at 60 °C with a substrate/catalyst molar ratio of 200 (Runs 1−5). π-Donating groups on the ring, such as a methoxy substituent in the *para* position, tended to enhance the reactivity of a substrate (cf. Run 4 with Run 1), while lower yields and conversions were obtained when an electron-withdrawing substituent, such as chloro, was present (Run 5). Alkylacetylenes were less reactive than arylacetylenes, so the reaction was carried out at 80 °C with a substrate/catalyst molar ratio of 100 (Runs 6−7). In some cases (Runs 5, 7), substrate conversion was not complete even after 15 h; prolonging the reaction time, however, to 24−36 h to achieve quantitative conversion was not accompanied by a significant improvement in the yield of **2**.

When phenylacetylene (**1a**) and *tert*-butylacetylene (**1g**) were employed, small amounts of furanones **3** were formed as byproducts (Runs 1 and 7, respectively); moreover, in the case of **1a**, a mixture of regioisomeric spiro derivatives **5a** (26% total yield) was also detected in the reaction mixture. All these byproducts were formed by competitive reductive carbonylation processes.[16] Unidentified high-molecular-mass products accounted for the substrate conversion in the examples reported in Runs 2−5 and 7.



5a

A very interesting feature of the present reaction is the effect exerted by an excess of CO_2 (40 atm) on promoting the overall oxidative carbonylation process leading to **2**. That carbon dioxide actually acted as a promoter, and not as a reagent, was unequivocally demonstrated by experiments carried out with $^{13}CO_2$, which showed that no significant ^{13}C incorporation occurred in the final product. The results obtained by carrying out the same experiments reported in Table 1, but in the absence of added CO_2, are shown in Table 2. As it can be seen from Table 2, the promoting effect of CO_2 was particularly striking in the case of arylacetylenes **1a−e** (cf. Runs 8−12 with Runs 1−5), and less important for alkylacetylenes **1f−g** (cf. Runs 13−14 with Runs 6−7). In fact, by working in the absence of CO_2, the yields of arylmaleic anhydrides dropped considerably (from 57−75% to 5−45%) in favor of the formation of furanone **3a** and spirolactones **5a** in the case of **1a** (Run 8), and of unidentified high-molecular mass products in the other cases (Runs 9−12).

The CO_2 effect can be interpreted on the basis of the reaction mechanism that leads to **2**. As we have already reported,[15−16] the carbonylation process is initiated by an I−Pd−CO_2H species (formed by H_2O attack on coordi-

Table 1. Synthesis of maleic anhydrides **2** by oxidative carbonylation of alk-1-ynes **1** in dioxane in the presence of PdI_2, KI (KI/PdI_2 molar ratio = 10), H_2O and CO_2; p(CO) = 16 atm, p(air) = 4 atm, $p(CO_2)$ = 40 atm; substrate concentration: 0.5 mmol/mL; t = 15 h

Run	**1**	R	H_2O/**1**/PdI_2	T [°C]	Conv. of **1** (%)[a]	Yield of **2** (%)[b]
1	**1a**	Ph	500:200:1	60	97	63 (58)[c]
2	**1b**	p-MeC_6H_4	200:200:1	60	90	75 (68)
3	**1c**	p-$tBuC_6H_4$	500:200:1	60	100	65 (56)
4[d]	**1d**	p-$MeOC_6H_4$	500:200:1	60	98	75 (70)
5	**1e**	p-ClC_6H_4	500:200:1	60	76	57 (49)
6	**1f**	Bu	200:100:1	80	98	96 (90)
7	**1g**	*t*Bu	200:100:1	80	73	48 (44)[e]

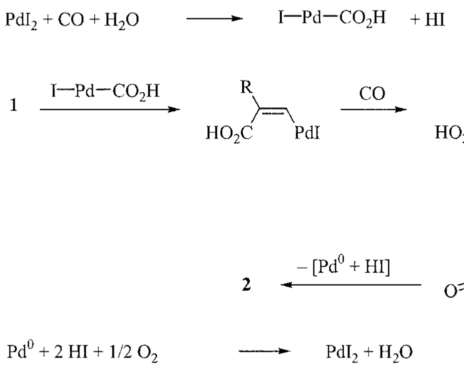
[a] Based on initial amount of **1**, by GLC. [b] GLC yield (isolated yield) based on **1**. [c] The reaction also led to the formation of 3-phenyl-5*H*-furan-2-one (**3a**) (4%) and a mixture of regioisomeric spiro derivatives **5a** (26%). [d] Reaction time was 8 h. [e] The reaction also led to the formation of 3-*tert*-butyl-5*H*-furan-2-one (**3g**) (4%).

Table 2. Effect of the absence of CO_2 on the reaction of alk-1-ynes **1** with CO, H_2O and O_2 in dioxane in the presence of PdI_2/KI (KI/PdI_2 molar ratio = 10); p(CO) = 16 atm, p(air) = 4 atm; substrate concentration.: 0.5 mmol/mL; t = 15 h

Run	1	R	H_2O/**1**//PdI_2	T [°C]	Conv. of **1** (%)[a]	Yield of **2** (%)[b]
8	**1a**	Ph	500:200:1	60	100	5 [c]
9	**1b**	p-MeC_6H_4	200:200:1	60	64	44
10	**1c**	p-$t$$BuC_6H_4$	500:200:1	60	100	35
11[d]	**1d**	p-$MeOC_6H_4$	500:200:1	60	86	45
12	**1e**	p-ClC_6H_4	500:200:1	60	64	37
13	**1f**	Bu	200:100:1	80	100	90[e]
14	**1g**	tBu	200:100:1	80	78	36[f]

[a] Based on initial amount of **1**, by GLC. [b] GLC yield based on **1**. [c] The reaction also led to the formation of 3-phenyl-5*H*-furan-2-one (**3a**) (12%) and a mixture of regioisomeric spiro derivatives **5a** (65%). [d] Reaction time was 8 h. [e] The reaction also led to the formation of 3-butyl-5*H*-furan-2-one (**3f**) (7%). [f] The reaction also led to the formation of 3-*tert*-butyl-5*H*-furan-2-one (**3g**) (6%).

nated CO), which then inserts the triple bond and CO to give the acylpalladium intermediate **I**. Tautomerization of the latter leads to the π-allylpalladium complex **II**, from which **2** is formed by [Pd^0 + HI] elimination from the H−O−C−PdI unit. (Scheme 1; anionic iodide ligands are omitted for clarity).



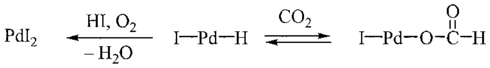
Scheme 1

Pd^0 is then reoxidized according to the usual mechanism[17] involving oxidative addition of I_2, which is formed in turn by oxidation of HI with oxygen. Palladium hydride complexes, however, can also be formed under the reaction conditions. In fact, an I−Pd−H species equilibrates with Pd^0 and HI deriving from the oxidative process leading to **2** [Equation (6)]; moreover, it can be formed by decarboxylation of I−Pd−CO_2H intermediates [Equation (7)].

$$Pd^0 + HI \rightleftharpoons I{-}Pd{-}H \quad (6)$$

$$I{-}Pd{-}CO_2H \longrightarrow I{-}Pd{-}H + CO_2 \quad (7)$$

In contrast to the situation we have already observed in alcoholic solvents under oxidative carbonylation conditions,[17−18] this I−Pd−H species is apparently rather stable in dioxane and can be responsible for side reactions leading to reductive-carbonylation products **3** and **5a**[15−16] and to unidentified high-molecular-mass products obtained when the reaction is carried out in the absence of CO_2. This particular stability is probably associated to the fact that the equilibrium according to Equation (6) is much more favored in an aprotic, low-polararity solvent, such as dioxane, rather then in a polar, protic solvent, such as an alcohol, that interacts strongly with HI. In the presence of a large excess of CO_2, however, the concentration of H−Pd−I is lowered through the equilibrium shown in Scheme 2, which involves the formation of a palladium−formate species through insertion of CO_2 into the Pd−H bond. As reported in the literature,[19] this is the way that CO_2 usually inserts into a palladium−hydride bond. Our results mentioned above with $^{13}CO_2$ clearly show that the other possible mode of insertion, leading to a hydroxycarbonylapalladium species I−Pd−CO_2H, is not at work under our conditions, since it would lead to some ^{13}C incorporation into the final product, in contrast to what was actually observed.



Scheme 2

Synthesis of Maleic Acids 4

Our catalytic system also proved useful for the direct synthesis of maleic acids **4** when oxidative carbonylation of alk-1-ynes **1** was carried out using H_2O as co-solvent [Equation (5)]. The best results, in terms of substrate conversion rate and product yields, were obtained by using a 3:1 mixture DME/H_2O as the solvent (Table 3). Unprecedented catalytic efficiencies for this kind of reaction were obtained under these conditions.

Maleic and fumaric acids have previously been obtained as byproducts (5−35% yield, catalytic efficiencies not higher than 3.5 mol of product per mol of Pd used) in the reaction reported in ref.[3] leading mainly to maleic anhydrides **2**. To the best of our knowledge, the only other example of direct synthesis of maleic acids by oxidative car-

Table 3. Synthesis of maleic acids **4** by oxidative carbonylation of alk-1-ynes **1** in 3:1 DME/H_2O in the presence of PdI_2 and 10 equiv. of KI; **1**/PdI_2 molar ratio = 2000; p(CO) = 16 atm, p(air) = 4 atm; substrate concentration: 1 mmol/mL; T = 80 °C

Run	1	R	t [h]	Conv. of **1** (%)[a]	Yield of **4** (%)[b]	Molar ratio of **4**/PdI_2
15	**1a**	Ph	3	96	71 (75)[c]	1420
16[d]	**1a**	Ph	3	23	0	0
17	**1b**	p-MeC_6H_4	5	97	64 (63)[e]	1280
18	**1d**	p-$MeOC_6H_4$	3	100	63 (53)	1260
19	**1e**	p-ClC_6H_4	5	100	55 (48)	1100
20	**1f**	Bu	8	76	48 (41)[f]	960
21	**1g**	tBu	8	75	20 (17)	400

[a] Based on initial amount of **1**, by GLC. [b] GLC yield (isolated yield) based on **1**. [c] The reaction also led to the formation of **2a** (10%). During the purification procedure, **2a** converted into **4a**, so the isolated yield reported refers to the overall amount of carboxylic acid obtained. See Exp. Sect. for details. [d] The reaction was carried out under 60 atm of a 4:1:10 mixture of CO/air/CO_2. [e] The reaction also led to the formation of **2b** (7%). During the purification procedure, **2b** converted into **4b**, so the isolated yield reported refers to the overall amount of diacid obtained. See Exp. Sect. for details. [f] The product was a mixture with its (E) isomer [(Z)/(E) = 10:1].

bonylation of alk-1-ynes has been described by us, using the PdI_2/KI catalytic system, but in N,N-dimethylacetamide/water as the solvent and with phenylacetylene (**1a**) as the substrate.[17] Under those conditions, however, the yields and catalytic efficiencies obtained (27% yield of **4a** and 3% of phenylfumaric acid, starting with a **1a**/PdI_2 molar ratio of 1000) were significantly lower than those obtained in the present work.

Carboxylic acids **4** are clearly formed by attack of H_2O on the acylpalladium intermediate **I** [Equation (8)]. In contrast to the reaction leading to anhydrides **2** considered in the previous section, the use of an excess of carbon dioxide in this case tended to inhibit, rather than promote, the reaction (cf. Run 16 with Run 15). The latter result is understandable, since HI prefers to protonate water, rather than undergo oxidative addition to Pd^0, in a largely aqueous medium and, as a consequence, the equilibrium according to Equation (6) is shifted to the left and no promoting effect can take place. On the other hand, the inhibiting effect is easily explained by considering that CO_2 may effectively compete with the substrate for coordination to the palladium atom. In fact, palladium complexes with carbon dioxide, stabilized by suitable ligands, have been reported in the literature.[19]

$$\mathbf{I} + H_2O \longrightarrow \mathbf{4} + Pd^0 + HI \qquad (8)$$

Conclusions

In conclusion, we have shown that a very simple catalytic system, consisting of PdI_2 in conjunction with an excess of KI, is able to catalyze the oxidative dicarbonylation of alk-1-ynes **1** to either maleic anhydrides **2** or maleic acids **4** with high catalytic efficiencies. Reactions that are carried out in dioxane as the solvent in the presence of small amounts of water lead to maleic anhydrides, and are effectively promoted by an excess of CO_2. In contrast, the reactions carried out in DME with water as cosolvent afford maleic acids, and are inhibited by added CO_2.

Experimental Section

General: Melting points were determined with a Reichert Thermovar melting point apparatus and are uncorrected. Elemental analyses were carried out with a Carlo Erba Elemental Analyzer Mod. 1106. ^1H and ^{13}C NMR spectra were taken with a Bruker AC300 spectrometer using Me_4Si as internal standard and recorded at 300 and 75 MHz, respectively. Chemical shifts (δ) and coupling constants (J) are given in ppm and in Hz, respectively. IR spectra were taken with a Perkin−Elmer Paragon 1000 PC FT-IR spectrometer. Mass spectra were obtained using an HP 5972A GC-MS apparatus at 70 eV ionization voltage. All reactions were analyzed by TLC on silica gel 60 F_{254} or by GLC using a Shimadzu GC-14A gas chromatograph and capillary columns with polymethylsilicone + 5% phenylsilicone as the stationary phase (HP-5). Column chromatography was performed on silica gel 60 (Merck, 70−230 mesh). 1,4-Dioxane was distilled under nitrogen from sodium before use.

Preparation of Substrates: Starting materials phenylacetylene (**1a**), 1-ethynyl-4-methylbenzene (**1b**), 1-chloro-4-ethynylbenzene (**1e**), hex-1-yne (**1f**), and 3,3-dimethylbut-1-yne (**1g**) were commercially available and were used without further purification. 1-*tert*-Butyl-4-ethynylbenzene (**1c**)[20] and 1-ethynyl-4-methoxybenzene (**1d**)[21] were prepared according to literature procedures. $^{13}CO_2$ (^{13}C = 99%, ^{18}O = 6%) was purchased from Isotec Inc. (USA).

Typical Procedure for Oxidative Carbonylation of Alk-1-ynes 1 to Maleic Anhydrides 2 and Separation of Products: A 250-mL stainless steel autoclave was charged in the presence of air with PdI_2 (15.0 or 30.0 mg, 4.2×10^{-2} or 8.3×10^{-2} mmol), KI (70.0 or 138.0 mg, 0.42 or 0.83 mmol), a solution of **1** (8.3 mmol) in anhydrous dioxane (16.6 mL), and H_2O (see Table 1 for the H_2O/**1**/PdI_2 molar ratio, reaction temperature and reaction time for each substrate). While stirring, the autoclave was pressurized with CO_2 (40 atm), CO (up to 56 atm) and air (up to 60 atm), then heated at the required temperature for the required time. After cooling, the autoclave was degassed, the solvent was evaporated under reduced pressure, and the products separated by column chromatography (SiO_2): **2a**, **3a** and **5a** (mixture of regioisomers)[9] [hexane/EtOAc, 7:3 to 1:1; order of elution: **3a** (yield: 27 mg, 2%), **2a** (838 mg, 58%),

5a (220 mg, 18%)]; **2b** (hexane/EtOAc, 9:1; 1.06 g, 68%); **2c** (hexane/EtOAc, 9:1; 1.07 g, 56%); **2d** (hexane/EtOAc, 8:2; 1.19 g, 70%); **2e** (hexane/EtOAc, 9:1; 848 mg, 49%); **2f** (hexane/EtOAc, 8:2; 1.15 g, 90%); **2g** (hexane/EtOAc, 8:2; 563 mg, 44%). Lactone **3g** could not be isolated owing to the very small amounts obtained (Table 1, Run 7), but was separated from the crude mixture derived from the reaction carried out in the absence of CO_2 (Table 2, Run 14) [hexane/EtOAc, 8:2; order of elution: **3g** (50 mg, 4%), **2g** (396 mg, 31%)]. Lactone **3f** was formed only from the reaction carried out in the absence of CO_2 (Table 2, Run 13) [hexane/EtOAc, 8:2; order of elution: **3f** (46 mg, 4%), **2f** (1.06 g, 83%)].

Typical Procedure for Oxidative Carbonylation of Alk-1-ynes 1 to Maleic Acids 4 and Separation of Products: A 250-mL stainless steel autoclave was charged in the presence of air with PdI_2 (2.0 mg, 5.6 $\times$ 10^{-3} mmol), KI (9.2 mg, 5.6 $\times$ 10^{-2} mmol), a solution of **1** (11.1 mmol) in DME (8.3 mL), and H_2O (2.8 mL). While stirring, the autoclave was pressurized with CO (up to 16 atm) and air (up to 20 atm), and then heated at 80 °C for the required time (see Table 3). After cooling, the autoclave was degassed and the solvent evaporated under reduced pressure. A 1 M solution of NaOH (25 mL) was added to the residue, and the mixture was heated at 75 °C for 1 h. After cooling, Et_2O was added and the phases were separated. The aqueous layer was washed 1−2 times with Et_2O, acidified with diluted sulfuric acid, and finally extracted several times with Et_2O. After drying with Na_2SO_4, the solvent was evaporated to give the product, which was dried in vacuo for several hours {**4a**: 1.60 g, 75%; **4b** 1.44 g, 63%; **4d**: 1.31 g, 53%; **4e**: 1.21 g, 48%; **4f** [10:1 (*Z*)/(*E*) mixture]: 784 mg, 41%; **4g**: 325 mg, 17%}.

3-Phenylfuran-2,5-dione (2a): Yield 838 mg, starting from 848 mg of **1a** (58%). Pale yellow solid, m.p. 118−119 °C (ref.[22] 119−120 °C). IR (KBr): $\tilde{\nu}$ = 3116 (w), 1821 (m), 1765 (s), 1611 (m), 1300 (w), 1226 (s), 1061 (w) 902 (m), 793 (m), 757 (m) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 7.00 (s, 1 H, =CH), 7.47−7.60 (m, 3 H aromatic), 7.94−7.99 (m, 2 H aromatic) ppm. ^{13}C NMR ($CDCl_3$): δ = 124.6, 126.9, 129.0, 129.4, 132.7, 146.8, 163.7, 164.6 ppm. MS: *m/z* = 174 (41) [M^+], 146 (1), 118 (3), 103 (9), 102 (100), 90 (3), 76 (10), 63 (6). $C_{10}H_6O_3$ (174.15): calcd. C 68.97, H 3.47; found C 69.01, H 3.45.

3-(4-Methylphenyl)furan-2,5-dione (2b): Yield 1.06 g, starting from 964 mg of **1b** (68%). Pale yellow solid, m.p. 106−108 °C (ref.[23] 108−109 °C). IR (KBr): $\tilde{\nu}$ = 1832 (w), 1757 (s), 1607 (m), 1231 (m), 902 (m), 829 (w) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 2.42 (s, 3 H, Me), 6.90 (s, 1 H, =CH), 7.27−7.33 (m, 2 H aromatic), 7.83−7.89 (m, 2 H aromatic) ppm. ^{13}C NMR ($CDCl_3$): δ = 21.7, 123.2, 124.2, 129.0, 130.1, 143.9, 146.6, 163.9, 164.8 ppm. MS: *m/z* = 188 (38) [M^+], 117 (10), 116 (100), 115 (71), 89 (8), 63 (10). $C_{11}H_8O_3$ (188.18): calcd. C 70.21, H 4.28; found C 70.89, H 4.26.

3-(4-*tert*-Butylphenyl)furan-2,5-dione (2c): Yield 1.07 g, starting from 1.31 g of **1c** (56%). Pale yellow solid, m.p. 106−107 °C. IR (KBr): $\tilde{\nu}$ = 2967 (m), 1837 (w), 1821 (w), 1768 (s), 1604 (m), 1232 (s), 930 (w), 904 (m), 843 (m) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 1.35 (s, 9 H, *t*Bu), 6.95 (s, 1 H, =CH), 7.50−7.56 (m, 2 H aromatic), 7.89−7.95 (m, 2 H aromatic) ppm. ^{13}C NMR ($CDCl_3$): δ = 31.0, 35.2, 123.3, 124.1, 126.4, 128.9, 146.7, 156.8, 164.0, 164.8 ppm. MS: *m/z* = 230 (< 0.5) [M^+], 223 (6), 205 (2), 167 (3), 150 (9), 149 (100), 104 (6), 93 (2), 76 (4), 65 (2), 57 (14). $C_{14}H_{14}O_3$ (230.26): calcd. C 73.03, H 6.13; found C 72.87, H 6.15.

3-(4-Methoxyphenyl)furan-2,5-dione (2d): Yield 1.19 g, starting from 1.10 g of **1d** (70%). Pale yellow solid, m.p. 142−143 °C (ref.[24] 143−144 °C). IR (KBr): $\tilde{\nu}$ = 1845 (w), 1833 (w), 1763 (s), 1606 (s), 1511 (m), 1265 (m), 1238 (s), 1180 (m), 1011 (w), 899 (m), 837 (m) cm^{-1}. ^1H NMR ([D_6]DMSO): δ = 3.85 (s, 3 H, OMe), 7.06−7.13 (m, 2 H aromatic), 7.54 (s, 1 H, =CH), 8.01−8.08 (m, 2 H aromatic) ppm. ^{13}C NMR ([D_6]acetone): δ = 56.0, 115.5, 121.0, 123.2, 132.0, 146.9, 164.0, 165.4, 166.5 ppm. MS: *m/z* = 204 (41) [M^+], 133 (10), 132 (100), 117 (25), 89 (23), 63 (12). $C_{11}H_8O_4$ (204.18): calcd. C 64.71, H 3.95; found C 64.88, H 3.97.

3-(4-Chlorophenyl)furan-2,5-dione (2e): Yield 848 mg, starting from 1.13 g of **1e** (49%). Pale yellow solid, m.p. 142−143 °C (ref.[25] 143−144 °C). IR (KBr): $\tilde{\nu}$ = 1852 (w), 1821 (w), 1765 (s), 1610 (w), 1491 (w), 1225 (s), 1093 (m), 902 (m), 839 (m) cm^{-1}. ^1H NMR ([D_6]DMSO): δ = 7.61−7.68 (m, 2 H aromatic), 7.78 (s, 1 H, =CH), 8.03−8.10 (m, 2 H aromatic) ppm. ^{13}C NMR ([D_6]acetone): δ = 122.9, 127.2, 130.2, 131.5, 138.7, 146.2, 164.9, 165.9 ppm. MS: *m/z* = 210 (8) [M^+ + 2], 208 (24) [M^+], 173 (4), 138 (33), 137 (10), 136 (100), 101 (15), 75 (13), 68 (8). $C_{10}H_5ClO_3$ (208.60): calcd. C 57.58, H 2.42, Cl 17.00; found C 57.41, H 2.41, Cl 16.96.

3-Butylfuran-2,5-dione (2f): Yield 1.15 g, starting from 682 mg of **1f** (90%). Pale yellow oil. IR (film): $\tilde{\nu}$ = 1842 (m), 1772 (s), 1641 (m), 1249 (s), 998 (w), 969 (w), 895 (m) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 0.96 (t, *J* = 7.3 Hz, 3 H, Me), 1.43 (sext, *J* = 7.3, 2 H, $CH_2CH_2CH_3$), 1.59−1.70 (m, 2 H, $CH_2CH_2CH_3$), 2.54 (td, *J* = 7.6, 1.7 Hz, 2 H, =$CHCH_2$), 6.63 (t, *J* = 1.7 Hz, 1 H, =CH) ppm. ^{13}C NMR ($CDCl_3$): δ = 166.0, 164.2, 153.9, 128.6, 29.0, 25.7, 22.3, 13.6 ppm. MS: *m/z* = 154 (< 0.5) [M^+], 126 (17), 112 (100), 111 (23), 84 (38), 81 (28), 67 (17). $C_8H_{10}O_3$ (154.16): calcd. C 62.33, H 6.54; found C 62.15, H 6.56.

3-*tert*-Butylfuran-2,5-dione (2g): Yield 563 mg, starting from 680 mg of **1g** (44%). Colorless solid, m.p. 70−72 °C. IR (KBr): $\tilde{\nu}$ = 2956 (m), 1837 (w), 1769 (s), 1737 (s), 1627 (w), 1461 (w), 1437 (w), 1369 (w), 1308 (w), 1264 (m), 1250 (m), 1199 (m), 1174 (m), 958 (m), 899 (s), 755 (w) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 1.35 (s, 9 H, *t*Bu), 6.54 (s, 1 H, =CH) ppm. ^{13}C NMR ($CDCl_3$): δ = 28.0, 33.3, 127.0, 161.5, 163.6, 164.2 ppm. MS: *m/z* = 154 (< 0.5) [M^+], 139 (8), 126 (72), 111 (47), 110 (43), 109 (22), 108 (16), 95 (71), 83 (53), 81 (38), 80 (18), 79 (18), 67 (100), 65 (22), 53 (18). $C_8H_{10}O_3$ (154.16): calcd. C 62.33, H 6.54; found C 62.28, H 6.57.

3-Phenylfuran-2(5*H*)-one (3a): Yield 27 mg, starting from 848 mg of **1a** (2%). Colorless solid, m.p. 86−87 °C (ref.[26] 84−86 °C). IR (KBr): $\tilde{\nu}$ = 1747 (vs), 1493 (w), 1441 (m), 1116 (s), 1059 (m), 956 (m), 791 (m), 740 (m), 691 (m), 656 (w), 522 (w) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 4.94 (d, *J* = 2.0 Hz, 2 H, CH_2), 7.37−7.46 (m, 3 H aromatic), 7.65 (t, *J* = 2.0 Hz, 1 H, =CH), 7.80−7.88 (m, 2 H aromatic) ppm. MS: *m/z* = 160 (36) [M^+], 132 (16), 115 (10), 104 (11), 103 (100), 77 (22), 63 (9), 51 (13). $C_{10}H_8O_2$ (160.17): calcd. C 74.99, H 5.03; found C 75.12, H 5.01.

3-Butylfuran-2(5*H*)-one (3f): Yield 46 mg, starting from 682 mg of **1f** (4%). Pale yellow oil. IR (film): $\tilde{\nu}$ = 2958 (s), 2931 (s), 2873 (m), 1750 (vs), 1652 (w), 1454 (m), 1337 (m), 1201 (m), 1111 (m), 1069 (s), 1041 (s), 835 (m) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 0.93 (t, *J* = 7.3 Hz, 3 H, Me), 1.32−1.45 (m, 2 H, CH_2CH_3), 1.50−1.62 (m, 2 H, $CH_2CH_2CH_3$), 2.26−2.34 (m, 2 H, $CH_2CH_2CH_2CH_3$), 4.76−4.79 (m, 2 H, CH_2O), 7.12−7.14 (m, 1 H, =CH) ppm. MS: *m/z* = 140 (5) [M^+], 125 (25), 111 (17), 98 (100), 95 (17), 79 (15), 69 (30), 55 (38). $C_8H_{12}O_2$ (140.18): calcd. C 68.55, H 8.63; found C 68.43, H 8.65.

3-*tert*-Butylfuran-2(5*H*)-one (3g): Yield 50 mg, starting from 680 mg of **1g** (4%). Colorless oil. IR (film): $\tilde{\nu}$ = 2960 (s), 2871 (m), 1753 (vs), 1641 (w), 1461 (m), 1365 (m), 1347 (w), 1311 (w), 1157 (m), 1063 (s), 1038 (m), 1007 (s), 953 (w), 831 (m), 786 (w) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 1.26 (s, 9 H, *t*Bu), 4.73 (d, *J* = 1.7, CH_2), 7.09 (t, *J* = 1.7 Hz, 1 H, =CH) ppm. MS: *m/z* = 140 (42) [M^+], 125 (55), 98 (36), 97 (84), 95 (39), 81 (42), 79 (100), 77 (27), 69 (41), 67 (48), 55 (47), 53 (56). $C_8H_{12}O_2$ (140.18): calcd. C 68.55, H 8.63; found C 68.66, H 8.62.

(*Z*)-2-Phenylbut-2-enedioic Acid (4a): Yield 1.60 g, starting from 1.13 g of **1a** (75%). Colorless solid, m.p. 115−116 °C. IR (KBr): $\tilde{\nu}$ = 3260−2435 (s, br), 1697 (vs), 1632 (s), 1427 (m), 1307 (m), 1214 (m), 1233 (m), 918 (m), 698 (m) cm^{-1}. ^1H NMR ([D_6]DMSO): δ = 6.39 (s, 1 H, =CH), 7.43−7.52 (m, 3 H aromatic), 7.54−7.64 (m, 2 H aromatic), 13.05 (br, 2 H, 2 CO_2H) ppm. ^{13}C NMR ([D_6]DMSO): δ = 117.0, 126.7, 129.1, 130.4, 133.5, 148.6, 166.1, 168.9 ppm. $C_{10}H_8O_4$ (192.17): calcd. C 62.50, H 4.20; found C 62.66, H 4.18.

(*Z*)-2-(4-Methylphenyl)but-2-enedioic Acid (4b): Yield 1.44 g, starting from 1.29 g of **1b** (63%). Pale yellow solid. IR (KBr): $\tilde{\nu}$ = 3310−2353 (s, br), 1726 (s), 1694 (s), 1603 (s), 1205 (s), 875 (m), 831 (m), 817 (m), 691 (m), 609 (m) cm^{-1}. ^1H NMR ([D_6]DMSO): δ = 2.33 (s, 3 H, Me), 6.33 (s, 1 H, =CH), 7.23−7.31 (m, 2 H aromatic), 7.43−7.51 (m, 2 H aromatic), 8.27 (br, 2 H, 2 CO_2H) ppm. ^{13}C NMR ([D_6]DMSO): δ = 20.8, 111.5, 126.5, 129.6, 140.3, 148.6, 166.0, 168.9 ppm. $C_{11}H_{10}O_4$ (206.19): calcd. C 64.08, H 4.89; found C 63.97, H 4.91.

(*Z*)-2-(4-Methoxyphenyl)but-2-enedioic Acid (4d): Yield 1.31 g, starting from 1.47 g of **1d** (53%). Pale yellow solid, m.p. 139−140 °C. IR (KBr): $\tilde{\nu}$ = 3250−2820 (s, br), 1746 (s), 1693 (s), 1597 (s), 1217 (s), 1181 (s), 1022 (w), 1009 (w), 832 (m), 603 (m) cm^{-1}. ^1H NMR ([D_6]acetone): δ = 3.86 (s, 3 H, OMe), 6.32 (s, 1 H, =CH), 6.98−7.06 (m, 2 H aromatic), 7.57−7.65 (m, 2 H aromatic), 8.0 (br, 2 H, 2 CO_2H) ppm. ^{13}C NMR ([D_6]acetone): δ = 55.8, 114.7, 115.3, 126.8, 129.3, 150.2, 162.5, 166.4, 169.3 ppm. $C_{11}H_{10}O_5$ (222.19): calcd. C 59.46, H 4.54; found C 59.77, H 4.56.

(*Z*)-2-(4-Chlorophenyl)but-2-enedioic Acid (4e): Yield 1.21 g, starting from 1.52 g of **1e** (48%). Pale yellow solid, m.p. 154−155 °C. IR (KBr): $\tilde{\nu}$ = 3170−2740 (s, br), 1714 (s), 1702 (s), 1633 (m), 1437 (m), 1303 (w), 1217 (s), 1093 (w), 923 (w), cm^{-1}. ^1H NMR ([D_6]acetone): δ = 5.52 (br, 2 H, 2 CO_2H), 6.43 (s, 1 H, =CH), 7.49−7.55 (m, 2 H aromatic), 7.64−7.70 (2 H aromatic) ppm. ^{13}C NMR ([D_6]acetone): δ = 118.5, 129.4, 130.0, 133.7, 136.6, 148.7, 166.0, 168.7 ppm. $C_{10}H_7ClO_4$ (226.61): calcd. C 53.00, H 3.11, Cl 15.64; found C 52.91, H 3.12, Cl 15.71.

2-Butylbut-2-enedioic Acid (4f) [10:1 (*Z*)/(*E*) Mixture]: Yield 784 mg, starting from 910 mg of **1e** (41%). Pale yellow solid. IR (KBr): $\tilde{\nu}$ = 3700−3100 (s, br), 1716 (s), 1705 (s), 1647 (m), 1421 (m), 1259 (m), 1214 (m), 896 (w) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 0.88−0.97 [m, 3 H, Me, isomer (*Z*) + 3 H, Me, isomer (*E*)], 1.31−1.60 [m, 4 H, $CH_2CH_2CH_3$, isomer (*Z*) + 4 H, $CH_2CH_2CH_3$, isomer (*E*)], 2.42 [t, *J* = 7.7 Hz, 2 H, $CH_2CH_2CH_2CH_3$, isomer (*Z*)], 2.79 [t, *J* = 7.4 Hz, 2 H, $CH_2CH_2CH_2CH_3$, isomer (*E*)], 5.88 [s, 1 H, =CH, isomer (*Z*)], 6.85 [s, 1 H, =CH (isomer *E*)], 9.77 [br., 2 H, 2 CO_2H (isomer *Z*) + 2 H, 2 CO_2H, isomer (*E*)]. $C_8H_{12}O_4$ (172.18): calcd. C 55.81, H 7.02; found C 55.69, H 7.00.

(*Z*)-2-*tert*-Butylbut-2-enedioic Acid (4g): Yield 325 mg, starting from 912 g of **1g** (17%). Pale yellow solid, m.p. 123−124 °C. IR (KBr): $\tilde{\nu}$ = 3300−2500 (s, br), 1731 (s), 1701 (s), 1645 (s), 1423 (s), 1271 (m), 1246 (w), 1219 (m), 881 (m) cm^{-1}. ^1H NMR ([D_6]DMSO): δ = 1.13 (s, 9 H, *t*Bu), 5.70 (s, 1 H, =CH), 12.43 (br, 2 H, 2 CO_2H) ppm. ^{13}C NMR ([D_6]DMSO): δ = 28.7, 34.7, 115.2, 160.2, 166.1, 169.3 ppm. $C_8H_{12}O_4$ (172.18): calcd. C 55.81, H 7.02; found C 55.73, H 6.99.

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