Triphenylphosphane-Mediated Addition of Dimethyl Acetylenedicarboxylate to 1,2- and 1,4-Benzoquinones: Synthesis of Novel γ-Spirolactones

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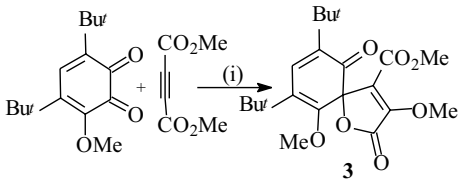
Dedicated to Professor Dr. Ivar Ugi in appreciation of his original contributions to organic chemistry

Abstract: The zwitterionic intermediate, generated by the addition of triphenylphosphane to dimethyl acetylenedicarboxylate, undergoes facile addition to *ortho*- and *para*-quinones to afford highly functionalized novel unsaturated γ-spirolactones in moderate to high yields.

Key words: addition reactions, dimethyl acetylenedicarboxylate, quinones, triphenylphosphane, spirolactones

Phosphorus and its compounds have been extensively used in organic synthesis.[1] Organophosphanes have received special attention and among the phosphanes, triphenylphosphane has emerged as the reagent of choice.[2] Its use as a catalyst in various isomerization reactions is well known.[3–5] It has been shown that triphenylphosphane adds to dimethyl azodicarboxylate to generate a zwitterion, which serves as intermediate in the Mitsunobu reaction and it has been trapped by propiolates to give dihydropyrazole derivatives.[6] Similarly, it has been shown by Tebby[7–13] that zwitterionic intermediates generated by the addition of triphenylphosphane to dimethyl acetylenedicarboxylate (DMAD), dicyanoacetylene, and dibenzoyl acetylene afford unique phosphorane derivatives. It is also known that such zwitterionic intermediates adds to benzaldehyde,[14] α-keto nitriles, and α-keto esters[15] to give γ-lactones. In the context of our interest in the cycloaddition chemistry of *o*-quinones,[16,17] especially the addition of dipolar species to *o*-quinones,[18] we undertook an investigation of the addition of zwitterionic intermediates generated from triphenylphosphane and dimethyl acetylenedicarboxylate to *o*-quinones. A preliminary report on the studies resulting in a spirolactone synthesis has already been published.[19] Subsequently, we have expanded these studies to include 1,4-quinones and our complete results are presented here.

Addition of the zwitterionic intermediate generated from triphenylphosphane (50 mol%) and DMAD to 4,6-di-*tert*-butyl-3-methoxy-1,2-benzoquinone afforded the spirolactone **3** in 70% yield. The reaction can be represented as in Scheme 1.



(i) Ph_3P/benzene, 80 °C, 4 h, 70%

Scheme 1

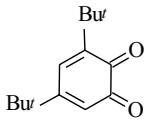
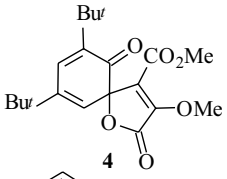
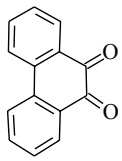
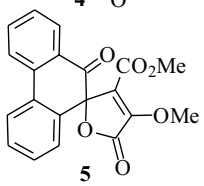
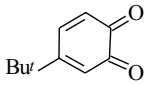
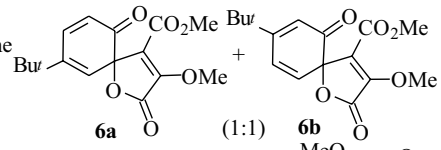
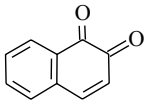
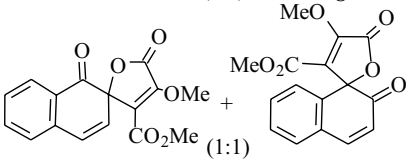
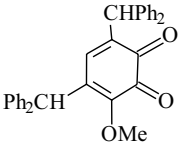
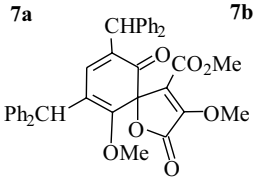
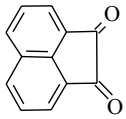
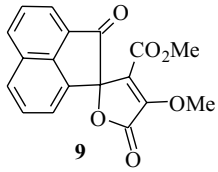
The IR spectrum of **3** showed strong absorption at ν = 1793 cm^{-1} and 1729 cm^{-1} due to the lactone and ester carbonyls, respectively. In the ^1H NMR spectrum, the three methoxycarbonyl H-atoms resonated at δ = 3.67 ppm as a singlet. The signals of the two methoxy groups were observed at δ = 3.60 ppm and 4.29 ppm as singlets. In the ^{13}C NMR spectrum of **3**, the spirocarbon resonated at δ = 83.3 ppm. The lactone and enone carbonyl carbons appeared at δ = 160.6 and 190.1 ppm, respectively. Final proof of the structure was discernible from the single crystal X-ray analysis of the adduct **4**.[19] Similar results were obtained with other *o*-quinones and these are summarized in Table 1.

4-*tert*-Butyl-1,2-benzoquinone on reaction with DMAD and triphenylphosphane afforded an inseparable mixture of isomers **6a** and **6b** in 1:1 ratio. In the ^1H NMR spectrum, the two *tert*-butyl groups resonated at δ = 1.17 ppm and 1.25 ppm and two signals at δ = 77.2 ppm and 78.4 ppm were attributed to spirocarbons in the ^{13}C NMR spectrum. The reaction of 1,2-naphthoquinone afforded a 1:1 mixture of spirolactones **7a** and **7b**. Compound **7a** showed absorptions in the IR spectrum at ν = 1795,1719, and 1695 cm^{-1} due to the lactone, ester, and benzoyl carbonyls. In the ^1H NMR spectrum, the olefinic H-atoms resonated at δ = 5.90 (d, 1 H, *J* = 10.6 Hz) and 6.91 (d, 1 H, *J* = 10.6 Hz) as two doublets. **7b** showed IR absorptions at ν = 1779, 1709, and 1681 cm^{-1}. In the ^1H NMR spectrum, the olefinic H-atoms were discernible at δ = 6.41 (d, 1 H, *J* = 11 Hz) and 7.50 (d, 1 H, *J* = 11 Hz) confirming an enone moiety.

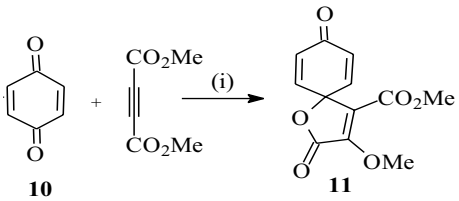
In continuation of the above investigations, we have also studied the reactivity of *p*-quinones towards the zwitterionic intermediate and the results are discussed in the following section. 1,4-Benzoquinone, when treated with DMAD and 50 mol% of triphenylphosphane in benzene at ambient temperature for 12 hours, afforded **11** in 88% yield (Scheme 2).

The structure of **11** was established by analytical and spectroscopic methods. The IR spectrum of **11** showed a strong absorption at ν = 1774 cm^{-1}, indicating the pres-

Table 1 Addition of Dimethyl Acetylenedicarboxylate to 1,2-Quinones

Entry	Quinone	Conditions	Product(s)	Yield (%)[a]
1		Benzene 80° C 48 h	 **4**	48[b]
2		Benzene 80° C 1 h	 **5**	78
3		Benzene 80° C 5 h	 **6a** (1:1) **6b**	26[c]
4		Benzene 80° C 4 h	 **7a** (1:1) **7b**	46
5		Benzene 80° C 1.5 h	 **8**	46
6		Benzene 80° C 1 h	 **9**	55

[a] Isolated yield.
[b] Yield based on recovered quinone was 60%, see Ref. 19.
[c] Inseparable mixture.

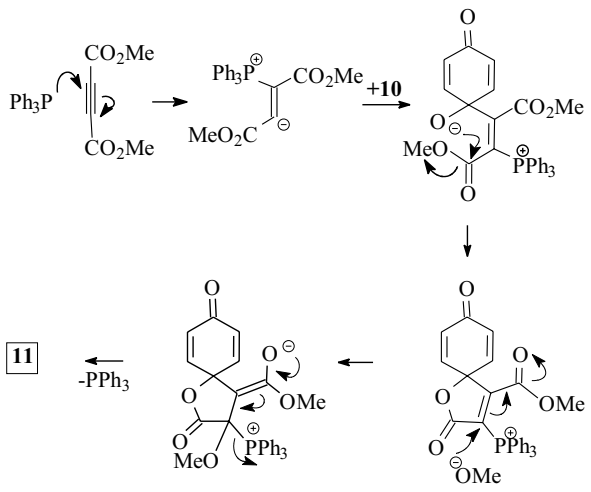


10 **11**

(i) Ph_3P/benzene, r.t., 12 h, 88%

Scheme 2

ence of the lactone moiety. In the ^1H NMR spectrum, the methoxycarbonyl group was observed as a singlet at $\delta = 3.73$ ppm and the methoxy group adjacent to the lactone carbonyl resonated at $\delta = 4.31$ ppm. The four olefinic H-atoms in the cyclohexadienone ring appeared as a multiplet between $\delta = 6.37-6.54$ ppm. In the ^{13}C NMR spectrum, the spirocarbon was discernible at $\delta = 76.9$ ppm. A mechanistic pathway for the formation of **11** involves the initial generation of a zwitterionic intermediate from triphenylphosphane and dimethyl acetylenedicarboxylate, which then adds to quinone carbonyl to yield a betaine. The betaine on subsequent cyclization leads to the spiro-



Scheme 3

lactone (Scheme 3). Similar spirolactones were obtained with other 1,4-quinones and these results are presented in Table 2

In conclusion, we have exploited the reactivity of both *ortho*- and *para*-quinones towards the zwitterionic intermediate generated by the addition of triphenylphosphane to DMAD. These investigations have resulted in a facile synthesis of highly functionalized unsaturated spirolactones. It is noteworthy that the unsaturated spirolactone moiety is present in a number of biologically active natural products such as chlorothricin, kijanolide, and tetranolide.[20]

Melting points were recorded on Toshniwal and Büchi melting point apparatus and are uncorrected. IR spectra were recorded on Perkin-Elmer-882 and Nicolet Impact 400D FT-IR spectrophotometers. NMR spectra were recorded on Jeol EX-90, Bruker-300, and Varian 500 NMR spectrometers. NMR spectra were obtained using $CDCl_3$ as the solvent and chemical shifts are given in δ scale with TMS as the internal standard. *J* values are given in Hz. Mass spectra were recorded on a Fisons GC-8000-MD-800 and AE1 MS-50-(IE) mass spectrometers. Elemental analyses were obtained on a Perkin-Elmer-2400 elemental analyzer. Purification by gravity column chromatography was carried out using silica gel (100-200 mesh). Hexanes and EtOAc were used as eluents. Dimethyl acetylenedicarboxylate was purchased from Aldrich Chemical Co. and was used without further purification.

7,9-Di-*tert*-butyl-3,6-dimethoxy-2,10-dioxo-1-oxaspiro[4.5]deca-3,6,8-triene-4-carboxylic Acid Methyl Ester (3)

To a mixture of 4,6-di-*tert*-butyl-3-methoxy-1,2-benzoquinone (100 mg, 0.4 mmol) and DMAD (68 mg, 0.48 mmol) in refluxing anhyd benzene (5 mL) was added Ph_3P (52 mg, 0.2 mmols) and the reflux was continued for 4 h. After removal of the solvent the residue was purified by chromatography on silica gel using 90:10 hexanes/EtOAc to afford **3** as a viscous yellow oil (107 mg, 70%).

IR (KBr): ν = 1793 (OC=O), 1729 (CO_2Me), 1681 (C=O), 1655 cm^{-1} (C=C).

^1H NMR: δ = 1.21 (s, 9 H, *t*-C_4H_9), 1.27 (s, 9 H, *t*-C_4H_9), 3.60 (s, 3 H, OCH_3), 3.67 (s, 3 H, CO_2CH_3), 4.29 (s, 3 H, =$COCH_3$), 7.12 (s, 1 H, =CH).

^{13}C NMR: δ = 29.0, 29.8, 34.6, 35.0, 51.8, 60.3, 62.1, 83.3, 121.7, 127.6, 131.8, 140.0, 150.0, 152.3, 166.6, 190.1.

EIMS: *m*/*z* (%) = 392 (M^+, 6), 349 (23), 348 (62), 333 (71), 301 (74), 271 (23), 245 (18), 143 (29) 115 (29), 91 (28), 59 (32), 57 (100), 44 (70).

7,9-Di-*tert*-butyl-3-methoxy-2,10-dioxo-1-oxaspiro[4.5]deca-3,6,8-triene-4-carboxylic Acid Methyl Ester (4)

See Ref. 19 for the experimental, spectral, and single crystal X -ray data.

Spiro[phenanthrenylene-1(2*H*), 3-methoxy-4-methoxycarbonylfuran-2-one]-2-one (5)

To a mixture of 9,10-phenanthrenequinone (230 mg, 1.10 mmol) and DMAD (172 mg, 1.21 mmol) in anhyd benzene (10 mL) at 80 °C was added Ph_3P (145 mg, 0.55 mmol) and the mixture was heated for further 1 h. The solvent was removed under reduced pressure and the residue, after chromatographic separation on silica gel using 80:20 hexanes/EtOAc gave **5** as a yellow solid (304 mg, 78%).

IR (KBr): ν = 1780 (OC=O), 1734 (CO_2Me), 1707 (C=O), 1657 cm^{-1} (C=C).

^1H NMR: δ = 3.40 (s, 3 H, CO_2CH_3), 4.36 (s, 3 H, =$COCH_3$), 7.25−7.50 (m, 4 H, ArH), 7.69−7.75 (m, 1 H, ArH), 8.04−8.13 (m, 3 H, ArH).

^{13}C NMR: δ = 52.0, 60.4, 81.0, 123.3, 123.6, 124.1, 128.1, 128.1, 128.7, 129.3, 130.4, 131.3, 131.9, 135.7, 136.6, 149.2, 160.7, 166.4, 190.1.

Anal. calcd for $C_{20}H_{14}O_6$: C, 68.57; H: 4.02. Found C, 68.82; H, 4.27.

7-*tert*-Butyl-3-methoxy-2,10-dioxo-1-oxaspiro[4.5]deca-3,6,8-triene-4-carboxylic Acid Methyl Ester (6a) and 8-*tert*-Butyl-3-methoxy-2,6-dioxo-1-oxaspiro[4.5]deca-3,6,8-triene-4-carboxylic Acid Methyl Ester (6b)

To a mixture of 4-*tert*-butyl-1,2-benzoquinone (500 mg, 3.05 mmol) and DMAD (520 mg, 3.66 mmol) in anhyd benzene (10 mL) at 80 °C was added Ph_3P (400 mg, 1.52 mmol) and the mixture was refluxed for 5 h. Chromatography on silica gel using 80:20 hexanes/EtOAc afforded an inseparable mixture of the spirolactones **6a** and **6b** as a viscous yellow oil (242 mg, 26%).

IR (KBr): ν = 1782 (OC=O), 1729 (CO_2Me), 1676 (C=O), 1656 cm^{-1} (C=C).

^1H NMR: δ = 1.17 (s, 9 H), 1.25 (s, 9 H), 3.68 (s, 6 H), 4.31 (s, 6 H), 5.71 (d, 1H, *J* = 1.9 Hz), 6.03 (d, 1 H, *J* = 10.0 Hz), 6.12 (s, 1 H), 6.25 (d, 1 H, *J* = 10.2 Hz), 6.61 (d, 1 H, *J* = 10.1 Hz),7.19−7.23 (dd, 1 H, *J* = 10.1, 1.8 Hz).

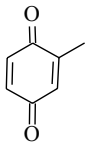
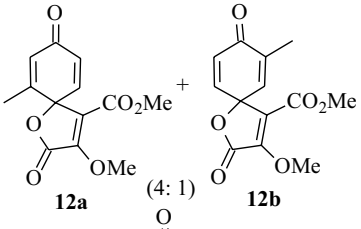
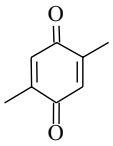
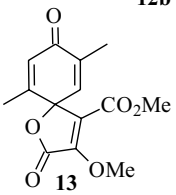
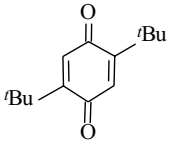
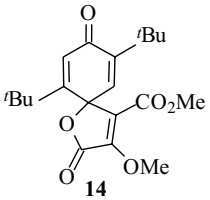
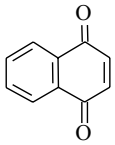
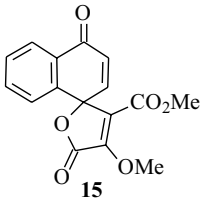
^{13}C NMR: δ = 27.9, 28.3, 34.7, 35.7, 51.8, 51.9, 60.0, 77.2 78.4, 119.2, 125.0, 125.6, 128.42, 132.9, 141.9, 147.5, 149.6, 160.6, 163.7, 165.9, 192.3, 192.4.

EIMS: *m*/*z* (%) = 306 (M^+, 36), 291 (9), 277 (27), 274 (20), 262 (19), 259 (100), 247 (61), 231 (45), 203 (26), 175 (19), 163 (21), 147 (14), 135 (22), 115 (42), 91 (63), 79 (39), 77 (54), 65 (27), 59 (68).

Spiro[naphthylene-1(2*H*),3-methoxy-4-methoxycarbonylfuran-2-one]-8-one (7a) and Spiro[naphthylene-1(2*H*),3-methoxy-4-methoxycarbonylfuran-2-one]-2-one (7b)

To a refluxing mixture of 1,2-naphthoquinone (125 mg, 0.79 mmol) and DMAD (135 mg, 0.95 mmol) in anhyd benzene (5 mL) was added Ph_3P (104 mg, 0.39 mmol) and heating was continued at

Table 2 Addition of Dimethyl Acetylenedicarboxylate to 1,4-Quinones

Entry	Quinone	Conditions	Product(s)	Yield(%)[a]
1		Benzene RT, 12 h	 **12a** (4: 1) **12b**	89
2		Benzene RT, 12 h	 **13**	73 (91)[b]
3		Benzene RT, 24 h	 **14**	26 (39)
4		Benzene 80 °C, 24 h	 **15**	26 (66)

[a] Isolated yield.
[b] Yield based on recovered quinone in parenthesis.

80 °C for 4 h. The solvent was evaporated and the residue was separated by radial chromatography on a Chromatotron® using 90:10 hexanes/EtOAc afforded **7a** as a yellow solid (54 mg, 23%). Further elution with the same solvent mixture afforded the spirolactone **7b** also as a yellow solid (55 mg, 23%).

7a

IR (KBr): ν = 1795 (OC=O), 1719 (CO_2Me), 1695 (C=O), 1663 cm^{-1} (C=C).

^1H NMR: δ = 3.55 (s, 3 H, CO_2CH_3), 4.30 (s, 3 H, =$COCH_3$), 5.90 (d, 1 H, *J* = 10.6 Hz, =CH), 6.91 (d, 1 H, *J* = 10.6 Hz, =CH), 7.25–7.75 (m, 3 H, ArH), 8.00 (dd, 1 H, *J* = 7.9, 1.3 Hz, ArH).

^{13}C NMR: δ = 52.0. 60.1, 79.0, 121.7, 126.9, 127.6, 128.4, 128.5, 129.0, 131.7, 135.4, 136.1, 149.3, 160.8, 166.0, 190.7.

EIMS: *m*/*z* (%) = 285 (M^+ − Me, 0.5), 284 (2.5), 256 (M^+ − CO_2, 75), 241 (M^+ − CO_2Me, 100).

7b

IR (KBr): ν = 1779 (OC=O), 1709 (CO_2Me), 1681 (C=O), 1658 cm^{-1} (C=C).

^1H NMR: δ = 3.52 (s, 3 H, CO_2CH_3), 4.31 (s, 3 H, =$COCH_3$), 6.41 (d, 1 H, *J* = 11 Hz, C=CH), 7.44 (m, 4 H, ArH), 7.53 (d, 1 H, *J* = 11 Hz, CH=C).

^{13}C NMR: δ = 52.0, 60.1, 79.0, 126.6, 127.0, 128.4, 129.0, 131.8, 135.4, 136.1, 145.7, 149.1, 160.5, 166.2, 190.7.

EIMS: *m*/*z* (%) = 285 (M^+ − Me, 18), 284 (100), 254 (14), 253 (61), 226 (30), 223 (26), 195 (24), 166 (11), 139 (46), 138 (32), 126 (26), 86 (15), 63 (8), 59 (9).

7,9-Bis(diphenylmethyl)-3,6-dimethoxy-2,10-dioxo-1-oxa-spiro[4.5]deca-3,6,8-triene-4-Carboxylic Acid Methyl Ester (8)

To a mixture of 3-methoxy-4,6-bis(diphenylmethyl)-1,2-benzoquinone (250 mg, 0.53 mmol) and DMAD (108 mg, 0.76 mmol) in refluxing anhyd benzene was added Ph_3P (70 mg, 0.26 mmol) and the mixture was stirred for 1.5 h. Chromatography of the residue on silica gel using 80:20 hexanes/EtOAc afforded **8** as yellow crystals (125 mg, 46%).

IR (KBr): ν = 1782 (OC=O), 1732 (CO_2Me), 1685 (C=O), 1655 cm^{-1} (C=C).

^1H NMR: δ = 3.45 (s, 3 H, OCH_3), 3.59, (s, 3 H, CO_2CH_3), 4.28 (s, 3 H, =$COCH_3$), 5.36 (s, 1 H, C*H*Ph_2), 5.59 (s, 1 H, C*H*Ph_2), 6.52 (s, 1 H, =CH), 6.90–7.02 (m, 8 H, ArH), 7.14–7.24 (m, 12 H, ArH).

^{13}C NMR: δ = 48.0, 49.0, 51.9, 52.4, 60.4, 63.2, 81.5, 120.2, 126.2, 126.5, 126.5, 126.9, 126.9, 128.2, 128.4, 128.5, 128.7, 128.9, 136.2, 141.2, 141.3, 144.4, 150.3, 152.0, 160.2, 166.1, 190.2.

Spiro[acenaphthylene-1(2*H*),3-methoxy-4-methoxycarbonylfuran-2-one]-2-one(9)

To a mixture of acenaphthenequinone (364 mg, 2.0 mmol) and DMAD (625 mg, 4.4 mmol) in anhyd benzene (15 mL) at 80 °C was added Ph_3P (262 mg, 1.0 mmol) and the mixture was stirred for 1 h. The residue on chromatographic separation on silica gel using 75:25 hexanes/EtOAc gave the spirolactone **9** as a white solid (353 mg, 55%); mp 121−122 °C (benzene/hexanes).

IR (KBr): ν = 1780 (OC=O), 1735 (CO_2Me), 1705 (C=O), 1653 cm^{-1} (C=C).

^1H NMR: δ = 3.37 (s, 3 H, CO_2CH_3), 4.41 (s, 3 H, =$COCH_3$), 7.50 (d, 1 H, *J* = 6.88 Hz, ArH), 7.64−7.70 (m, 1 H, ArH), 7.77−7.82 (m, 1 H, ArH), 8.01 (d, 1 H, *J* = 8.3 Hz, ArH), 8.08 (d, 1 H, *J* = 6.9 Hz, ArH), 8.20 (d, 1 H, *J* = 8.1 Hz, ArH).

^{13}C NMR: δ = 52.0, 60.3, 85.2, 121.2, 123.1, 127.2, 128.5, 130.8, 132.3, 143.2, 149.3, 160.8, 165.8, 195.0.

EIMS: *m*/*z* (%) = 325 (M^+ + 1, 1.7), 324 (M^+, 8.9), 309 (1), 280 (11), 265 (100), 237 (31), 194 (15), 179 (15), 150 (30), 138 (23), 126 (21), 75 (13), 59 (16), 44 (22).

3-Methoxy-2,8-dioxo-1-oxaspiro[4.5]deca-3,6,9-triene-4-carboxylic Acid Methyl Ester (11)

A mixture of 1,4-benzoquinone (500 mg, 4.63 mmol) DMAD (790 mg, 5.56 mmol) in anhyd benzene (10 mL) was purged with argon and stirred at r.t. To this Ph_3P (606 mg, 2.31 mmols) was added and the mixture was stirred for 12 h. Removal of the solvent and chromatography on silica gel using 80:20 hexanes/EtOAc afforded **11** as colorless prisms (1.022 g 88%); mp 120−122 °C (benzene/hexanes).

IR (KBr): ν = 1774 (OC=O), 1727 (CO_2Me), 1680 (C=O), 1647 cm^{-1} (C=C).

^1H NMR: δ = 3.73 (s, 3 H, CO_2CH_3), 4.31 (s, 3 H, =$COCH_3$), 6.37−6.54 (m, 4 H, CH=CH).

^{13}C NMR: δ = 52.3. 60.3, 76.9, 120.6, 131.5, 142.2, 149.8, 160.3, 164.8, 184.1.

Anal. calcd for $C_{12}H_{10}O_6$: C, 57.61; H, 4.03. Found C: 57.53; H, 4.06.

3-Methoxy-7-methyl-2,8-dioxo-1-oxaspiro[4.5]deca-3,6,9-triene-4-carboxylic Acid Methyl Ester (12a) and 3-Methoxy-6-methyl-2,8-dioxo-1-oxa-spiro[4.5]deca-3,6,9-triene-4-carboxylic Acid Methyl Ester (12b)

To a mixture of 2-methyl-1,4-benzoquinone (500 mg, 4.1 mmol) and DMAD (700 mg, 4.9 mmol) in anhyd benzene (10 mL) was added Ph_3P (540 mg, 2.05 mmol) under argon at r.t. during 12 h. The solvent was removed and the residue on radial chromatography with 90:10 hexanes/EtOAc afforded **12a** as white needles (198 mg, 18%); mp 116−118 °C (benzene/ hexanes). Further elution gave **12b** as a white solid (775 mg, 71%); mp 112−113 °C (benzene/hexanes).

12a

IR (KBr): ν = 1782 (OC=O, sharp), 1769 (OC=O, weak), 1719 (CO_2Me), 1677 cm^{-1} (C=O).

^1H NMR: δ = 1.82 (d, 3 H, *J* = 1.39, CH_3), 3.71 (s, 3 H, CO_2CH_3), 4.30 (s, 3H, =$COCH_3$), 6.28 (t, 1 H, *J* = 1.4, =CH), 6.36 (dd, 1 H, *J* = 9.9, 1.7 Hz, =CH), 6.45 (d, 1 H, *J* = 9.9, =CH).

^{13}C NMR: δ = 17.1. 52.5, 60.4, 78.9, 121.2, 130.0, 131.3, 142.4, 149.8, 150.9, 160.4, 165.2, 184.8.

Anal. calcd for $C_{13}H_{12}O_6$: C, 59.09; H, 4.58. Found C, 59.53; H, 4.37.

12b

IR (KBr): ν = 1768 (OC=O), 1707 (CO_2Me), 1676 cm^{-1} (C=O).

^1H NMR: δ = 1.94 (d, 3 H, *J* = 1.43 Hz, CH_3), 3.72 (s, 3 H, CO_2CH_3), 4.30 (s, 3 H, =$COCH_3$) 6.25 (t, 1 H, *J* = 2.9 Hz, =CH), 6.38 (d, 1 H, *J* = 9.9 Hz, CH), 6.46 (dd, 1 H, *J* = 9.9, 2.8 Hz, =CH),

^{13}C NMR: δ = 15.8. 52.3, 60.2, 77.8, 121.1, 131.6, 137.1, 138.9, 142.0, 149.5, 160.5, 165.0, 184.9.

Anal. calcd for $C_{13}H_{12}O_6$: C, 59.09; H, 4.58. Found C, 59.23; H, 4.55.

3-Methoxy-6,9-dimethyl-2,8-dioxo-1-oxaspiro[4.5]deca-3,6,9-triene-4-carboxylic Acid Methyl Ester (13)

To a mixture of 2,5-dimethyl-1,4-benzoquinone (500 mg, 3.67 mmol) and DMAD (650 mg, 4.57 mmol) in anhyd benzene (10 mL) at r.t. under argon was added Ph_3P (482 mg, 1.84 mmol) and the mixture was stirred for 24 h. After the solvent was removed, the residue was chromatographed on silica gel. Elution with 95:5 hexanes/EtOAc removed the unreacted quinone (99 mg). Further elution gave **13** as colourless needles (752 mg, 73%). The yield based on the reacted quinone is 91%; mp 107−109 °C (CH_2Cl_2/hexanes).

IR (KBr): ν = 1778, 1764 (OC=O), 1719 ((CO_2Me), 1685 cm^{-1} (C=O).

^1H NMR: δ = 1.82 (d, 3 H, *J* = 1.4 Hz, CH_3), 1.93 (d, 3 H, *J* = 1.5 Hz, CH_3), 3.71 (s, 3 H, CO_2CH_3), 4.29 (s, 3 H, =$COCH_3$) 6.22−6.27 (dd, 2 H, *J* = 11.8, 1.4 Hz, =CH).

^{13}C NMR: δ = 15.3, 16.7, 52.4, 60.2, 79.6, 121.4, 129.8, 137.2, 138.5, 149.4, 150.5, 160.4, 165.4, 185.4.

EIMS: *m*/*z* (%) = 278 (M^+, 12), 246 (25), 235 (37), 219 (32), 203 (41), 191 (61), 175 (30), 163 (17), 147 (22), 131 (31), 103 (39), 77 (67), 59 (100), 51 (42).

Anal. calcd for $C_{14}H_{14}O_6$: C, 60.43; H, 5.07. Found C, 60.33; H, 5.1.

6,9-Di-*tert*-butyl-3-methoxy-2,8-dioxo-1-oxaspiro[4.5]deca-3,6,9-triene-4-carboxylic Acid Methyl Ester (14)

A mixture of 2,5-di-*tert*-butyl-1,4-benzoquinone (500 mg, 2.27 mmol) and DMAD (388 mg, 2.72 mmol) in anhyd benzene (10 mL) under argon was treated with Ph_3P (298 mg, 1.13 mmol) at r.t. and the mixture was stirred for 24 h. The residue obtained after the removal of the solvent was chromatographed on silica gel using 95:5 hexanes/EtOAc removed the unreacted quinone (251 mg) and further elution with 90:10 hexanes/EtOAc yielded **14** as light yellow crystals (214 mg, 26%); mp 121−123 °C (CH_2Cl_2/hexanes).

IR (KBr): ν = 1796 (OC=O), 1723 (CO_2Me) 1667 cm^{-1} (C=O).

^1H NMR: δ = 1.17 (s, 9 H, *t*-C_4H_9),1.21 (s, 9 H, t-C_4H_9), 3.66 (s, 3 H, CO_2CH_3), 4.25 (s, 3 H, =$COCH_3$), 5.91 (s, 1 H, =CH), 6.34 (s, 1 H, =CH).

^{13}C NMR: δ = 28.7, 30.8, 34.3, 37.2, 52.1, 60.0, 82.2, 123.4, 131.3,140.1, 146.9, 149.1, 157.2, 160.6, 165.8, 186.0.

Anal. calcd for $C_{20}H_{26}O_6$: C, 66.28; H, 7.25. Found C, 66.37; H, 7.48.

Spiro[naphthylene-1(2*H*),3-methoxy-4-methoxycarbonylfuran-2-one]4-one (15)

Ph_3P (420 mg, 1.60 mmol) was added to a refluxing mixture of 1,4-naphthoquinone (500 mg, 3.16 mmol) and DMAD (542 mg, 3.81 mmol) in anhyd benzene (10 mL) and the heating was continued for 4 h. The solvent was removed and the residue on chromatographic separatoin on silica gel using 95:5 hexanes/EtOAc removed the unreacted quinone (300 mg) and elution with 80:20 hexanes/EtOAc afforded the product **15** as light yellow crystals (250 mg, 26%); mp 180−182 °C. The yield based on the reacted starting material was 66%.

IR (KBr): ν = 1761 (OC=O), 1706 (CO_2Me), 1681 (C=O), 1643 cm^{-1} (C=C).

^1H NMR: δ = 3.54 (s, 3 H, CO_2CH_3), 6.60 (s, 2 H, =CH), 4.38 (s, 3 H, $=COCH_3$), 7.21 (d, 1 H, *J* = 7.6 Hz, ArH),7.50−7.62 (m. 2 H, ArH), 8.16 (dd, 1 H, *J* = 7.5, 1.0 Hz, ArH).

^{13}C NMR: δ = 52.2, 60.5, 78.4, 123.4, 127.1, 127.3, 129.7, 131.3, 131.8, 133.2, 136.8, 142.6, 149.3, 160.3, 165.7, 183.5.

Anal. calcd for $C_{16}H_{12}O_6$: C, 64.00; H, 4.03. Found C, 63.87; H, 3.99.

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