

Triphenylphosphine promoted addition of dimethyl acetylenedicarboxylate to 1,2-benzoquinones: facile synthesis of novel γ -spirolactones

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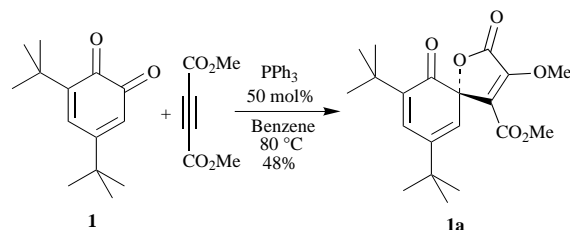
The addition of dimethyl acetylenedicarboxylate to *o*-quinones in the presence of triphenylphosphine leading to highly functionalised γ -spirolactones is reported.

Introduction

The stoichiometric as well as the catalytic use of phosphines and a variety of other organophosphorus compounds has become an integral part of organic synthesis.¹ In particular, triphenylphosphine (TPP) acts as a catalyst in various isomerization reactions of alkynes and allenes,² and in the nucleophilic addition of malonate to methyl propiolate.³ The addition of TPP to electron deficient alkynes, leading to zwitterionic compounds and the subsequent reactions of the latter species, notably dimerization, has been known from the work of Tebby and co-workers.⁴ Very recently dimethyl acetylenedicarboxylate (DMAD) has been reported to add to activated carbonyl compounds such as α -keto esters and α -keto nitriles under the influence of TPP to afford γ -lactones.^{5,†} In view of our general interest in the chemistry of *o*-quinones,⁶ we have examined the reaction of DMAD with *o*-quinones in the presence of TPP and our preliminary results are reported here.

Results and discussion

A mixture of 3,5-di-*tert*-butyl-1,2-benzoquinone **1** and DMAD when treated with 50 mol% of TPP at 80 °C in benzene for 24 h afforded 48% of the spirolactone **1a** (Scheme 1). The structure



Scheme 1

of the spirolactone **1a** was confirmed on the basis of spectral and analytical data and finally by X-ray crystallography (Fig. 1).[‡]

The spirolactone formation can be rationalized as shown in Scheme 2.

Similar results were obtained with a number of other *o*-quinones and these are summarised in Table 1.

[†] The addition of DMAD to benzaldehyde in the presence of triphenylphosphine leading to the formation of γ -butyrolactone in low yield was known from an earlier report.⁷

[‡] Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See instructions for Authors, *J. Chem. Soc., Perkin Trans. 1*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 207/149.

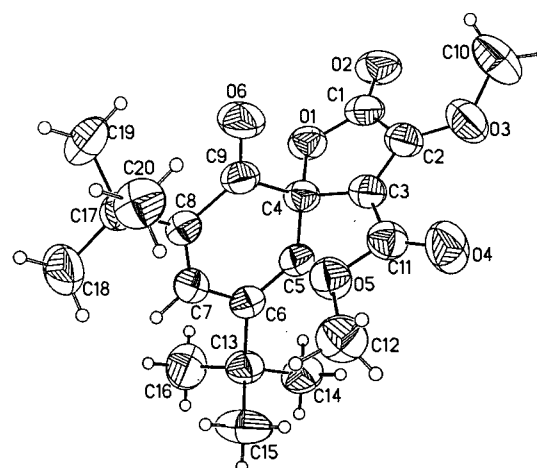
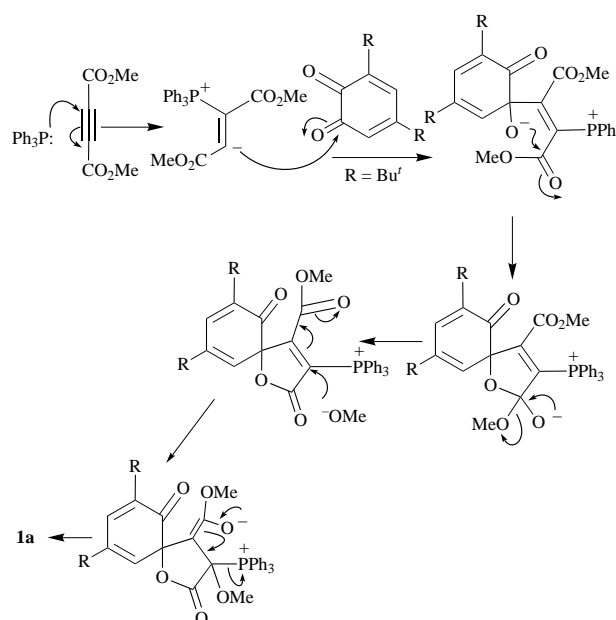


Fig. 1 X-Ray crystal structure of **1a**



Scheme 2

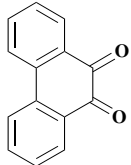
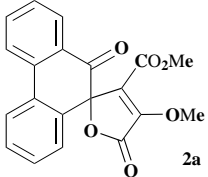
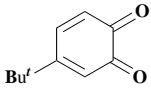
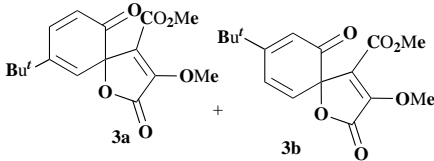
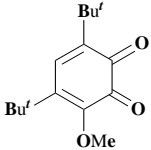
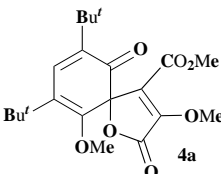
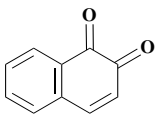
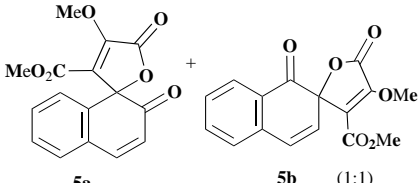
Conclusion

In conclusion we have found that the reaction of *o*-quinones with DMAD in the presence of TPP leads to a facile synthesis of highly functionalized spirolactones.

Experimental

All reactions were carried out in oven dried glassware at 110 °C. Silica gel chromatography was carried out using 100–200 mesh silica gel. Melting points were taken in a Toshniwal melting

Table 1 Reaction of various quinones with dimethyl acetylenedicarboxylate

Entry	Quinone	Conditions	Product(s)	Yield (%) ^a
2		Benzene 80 °C 1 h		75
3		Benzene 80 °C 5 h		26 ^b
4		Benzene 80 °C 4 h		70
5		Benzene 80 °C 8 h		46

^a Isolated yield. ^b Inseparable mixture.

point apparatus and are uncorrected. Light petroleum refers to the fraction boiling in the range 60–80 °C. IR spectra were recorded on a Perkin-Elmer 882 spectrometer. ¹H NMR spectra were recorded on a Varian Unity 500 NMR spectrometer at 500 MHz and JEOL EX-90 at 90 MHz with tetramethylsilane as internal standard. *J* values are given in Hz. ¹³C NMR spectra were recorded at 125 MHz (Varian Unity 500) and 22.5 MHz (JEOL EX-90). Mass spectra were recorded in AE1 MS-50-(IE) and elemental analyses were obtained on a Perkin-Elmer elemental analyser-2400.

General procedure

Methyl 3,5-di-tert-butyl-5',6-dioxo-4'-methoxyspiro[cyclohexa-2,4-diene-1,2'-(2',5'-dihydrofuran)]-3'-carboxylate. A mixture of 3,5-di-tert-butyl-1,2-benzoquinone **1** (0.440 g, 2.0 mmol) and dimethyl acetylenedicarboxylate (0.320 g, 2.2 mmol) was purged with argon at 80 °C in benzene (10 ml). To this mixture triphenylphosphine (0.262 g, 1.0 mmol) was added and the heating continued for 24 h. The solvent was removed under vacuum and the residue chromatographed on silica gel and the product eluted with an 80:20 light petroleum–ethyl acetate mixture to afford the spiro lactone **1a** (0.340 g, 48%, 60% based on reacted quinone); mp 130–132 °C (CH₂Cl₂–hexane) (Found: C, 65.92; H, 7.22; M⁺, 362. C₂₀H₂₆O₆ requires C, 66.28; H, 7.25%; *M*, 362); ν_{max}/cm^{−1} 2968, 2880, 1779 (CO–O–, lactone), 1738 (CO₂Me), 1684, 1660 (C=C–CO); δ_H (500 MHz; CDCl₃) 6.978–6.974 (d, 1H, *J* 2.0, C=CH), 5.644–5.640 (d, 1H, *J* 2.0, C=CH), 4.281 (s, 3H, C=C–OMe), 3.643 (s, 3H, CO₂Me), 1.228 (s, 9H, Bu'), 1.147 (s, 9H, Bu'); δ_C (125 MHz; CDCl₃) 192.114, 166.624, 160.923, 149.503, 147.889, 144.575, 135.959, 122.781, 80.306, 60.338, 51.927, 35.137, 35.001, 29.257, 28.527.

X-ray analysis of **1a**

The crystal used for X-ray study had dimensions of 0.4 × 0.4 × 0.35 mm. Crystal data: C₂₀H₂₆O₆ *M* = 362.41, triclinic,

space group, P $\bar{1}$, unit cell dimensions: *a* = 9.3827(7) Å, *b* = 9.7857(7) Å, *c* = 12.3881(7) Å, *a* = 97.993(5)°, *β* = 93.180(6)°, *γ* = 116.531(5)°, *V* = 998.85(12) Å³, *D*_C = 1.205 Mg m^{−3}, *T* = 298(2) K, *R* indices [*I* > 2σ(*I*)] = *R*₁ = 0.0496, *wR*₂ = 0.1366; number of unique reflections = 3421, λ = 1.54178 Å.

Data collection and processing. The intensities were measured on a Siemens P4 X-ray diffractometer using Cu-Kα radiation and 2θ–ω. Of the 7387 reflections collected, 3421 with *I* > 2σ(*I*) were used for structure determination and refinement.

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