Reaction of singlet oxygen with enolic tautomers of 1-aryl-2-methyl 1,3-diketones

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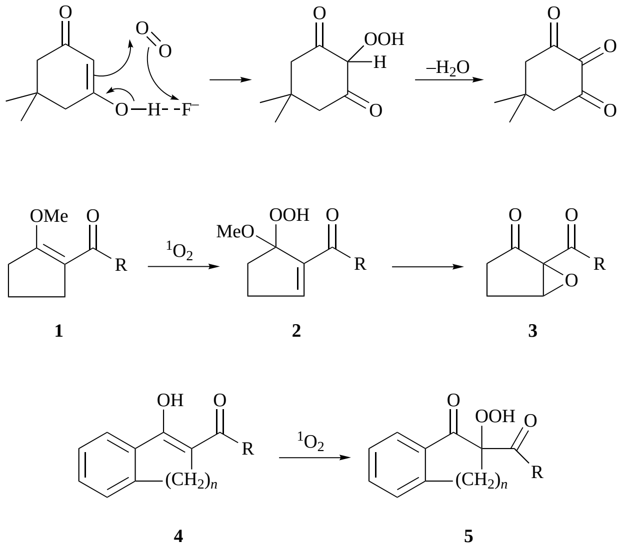
The 1-(2′,4′,6′-trialkylphenyl)-2-methyl 1,3-diketones 6 exist in the enol form in solution, and on reaction with singlet oxygen in acetonitrile give products arising from hydrogen abstraction from both the enolic hydroxy and the 2-methyl groups by the singlet oxygen; namely, the 2-hydroperoxy 1,3-diketones 7, the 2-methylene 1,3-diketones 8 and the epoxy ketones 9. The 2-hydroperoxy 1,3-diketones 7 readily undergo deoxygenation by triphenylphosphine to give the 2-hydroxy 1,3-diketones 12. In the reaction of 6 in methanol or ethanol, the initially formed enedione 8 reacts with the solvent to give the corresponding Michael adducts 10 and 11.

Singlet oxygen shows a diversity of reactions with substrates.[1] Since it is electrophilic, the reactions with α,β-unsaturated carbonyl compounds are often slow, but show marked regioselectivity; singlet oxygen abstracts hydrogen from an alkyl group geminal to the carbonyl group so that the entering oxygen bonds to the carbon away from the carbonyl group. Much work has been carried out in recent years on such regioselective singlet oxygenation of α,β-unsaturated ketones,[2] aldehydes,[3] acids,[3b,4] and esters.[3b,4b,5] However, the reactions of singlet oxygen with enolic tautomers of 1,3-dicarbonyl compounds, β-hydroxy-α,β-unsaturated carbonyls, have received little attention. Wasserman and Pickett reported that enolic tautomers of 1,3-dicarbonyl compounds reacted with singlet oxygen to produce 1,2,3-triketones[6] in the presence of fluoride ion which enhances the nucleophilicity of enols.[7] They postulated a 2-hydroperoxy 1,3-diketone as an intermediate in this reaction. Ensley *et al.* reported the regioselective photooxygenation of the β-alkoxy cyclic enones **1** to give the unsaturated hemiperketals **2** which decomposed to the epoxide **3**.[8] We have recently reported that the enolic tautomers **4** of acyl- and alkoxycarbonyl-benzocycloalkenones reacted with singlet oxygen to give 2-hydroperoxy 1,3-dicarbonyl compounds **5**[9] (Scheme 1). We report here that the reaction of the enolic tautomers **6** of 1-aryl-2-methyl 1,3-diketones in acetonitrile with singlet oxygen gives the 2-hydroperoxy 1,3-diketones **7**, the 2-methylene 1,3-diketones **8** and the epoxy ketones **9**. In the reaction of **6** in methanol or ethanol, the enedione **8** reacted with the solvent to give the corresponding Michael adducts **10** and **11**.

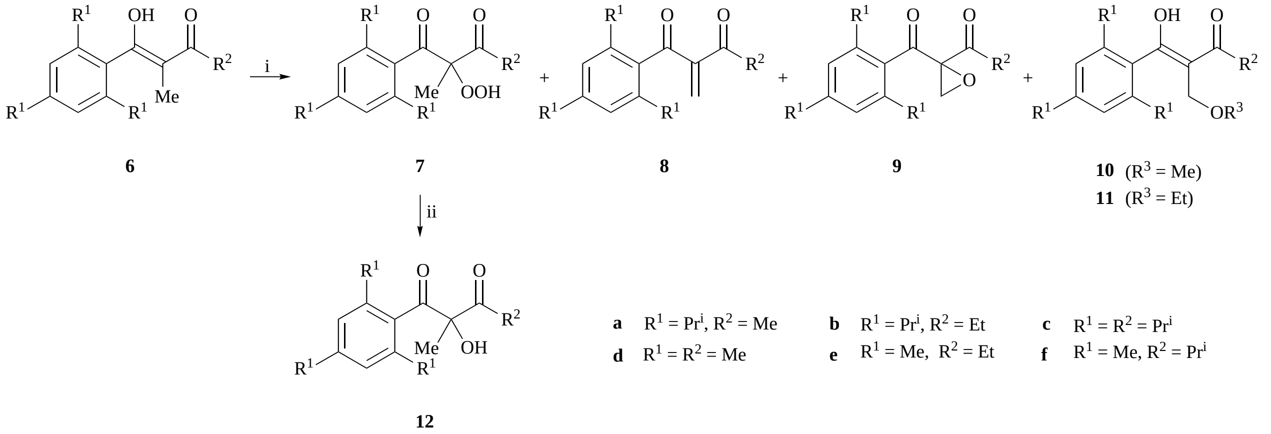


Scheme 1

Results and discussion

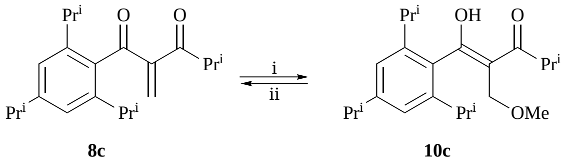
The 1-aryl-2-methyl 1,3-diketones were prepared by the reaction of 2′,4′,6′-trialkylpropiophenones with aldehydes, followed by oxidation of the resulting ketols.[10] The products were obtained as the enol form **6** after passage through a silica gel column followed by distillation or recrystallization.[11]

Irradiation at room temperature with a tungsten–halogen lamp (K_2CrO_4 solution filter) of 1-(2′,4′,6′-triisopropylphenyl)-2-methylbutane-1,3-dione **6a** in acetonitrile through which air was bubbled in the presence of Methylene Blue as a sensitizer gave the hydroperoxy ketone **7a**, the enedione **8a** and the epoxy ketone **9a**, in 35, 42 and 6% yield, respectively. Photooxidation of the compounds **6b**–**f** under the same conditions also gave the corresponding hydroperoxy ketones **7b**–**f**, the enediones **8b**–**f** and the epoxy ketones **9d**–**f**. The epoxy ketones **9b** and **9c** could not be detected. The reaction of **6** with singlet oxygen in alcoholic solvents gave different products from those in acetonitrile. Irradiation of a methanolic or ethanolic solution of **6a**–**c**,**e**,**f** under the same conditions gave **10a**–**c**,**e**,**f** or **11a** as the major product, along with the hydroperoxy ketones **7a**–**c**,**e**,**f** and the epoxy ketones **9a**,**b**,**e**,**f** (Scheme 2). The enedione **8** could not be detected. The structures of the products were assigned on the basis of their analytical and spectral data. The ^1H NMR spectrum of **7** showed a singlet at δ_H 8.9–9.9 due to OOH. The ^{13}C NMR spectrum of **7** showed two carbonyl carbons in the range δ_C 200–211 and a quaternary carbon due to C-2 at δ_C 96–99. Deoxygenation of **7a**,**c**–**e** with triphenylphosphine gave the corresponding alcohols **12a**,**c**–**e** which showed a hydroxy ^1H NMR peak at δ_H 4.4–4.8. The ^1H NMR spectrum of **8** showed an AB pair at δ_H 5.8–5.9 and 6.4–6.6 due to two olefinic protons. The ^{13}C NMR spectrum of **8** showed two peaks due to carbonyl carbons in the range δ_C 198–207 and eight aromatic and olefinic sp^2 carbons in the range δ_C 121–151. The compounds **8d**–**f** were isolated as oils of high purity as determined on the basis of their NMR spectra. However, distillation for microanalysis



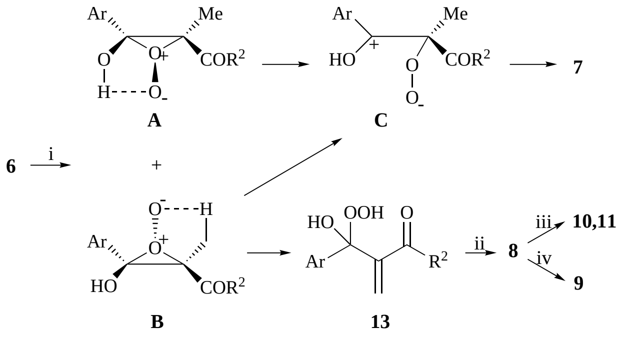
Scheme 2 *Reagents*: i, $^1O_2$/MeCN, MeOH or EtOH; ii, PPh_3

could not be achieved because they underwent thermal decomposition. The compounds **8a–c** were obtained as crystals. The compounds **10a–c**,**e** and **11a** were obtained as oils, but distillation for microanalysis could not be achieved because they were transformed into **8a–c**,**e** by loss of alcohols (Scheme 3). The ^{13}C NMR spectra of **10a–c**,**e**,**f** and **11a** showed eight aromatic and olefinic sp^2 carbons, indicating that they existed in the enol form.



Scheme 3 *Reagents*: i, MeOH; ii, heat

Photooxidation of the enols **6** probably takes place through the ene reaction with $^1O_2$, where oxygen abstracts hydrogen from either the enolic hydroxy group or the 2-methyl group. The hydroperoxy ketone **7** would arise as a result of hydrogen abstraction from the enolic hydroxy group. The compounds **8**, **9**, **10** and **11** would be produced *via* the hydroperoxide **13** formed through hydrogen abstraction from the 2-methyl group. The hydroperoxide **13** would decompose to afford the enedione **8** with loss of hydrogen peroxide. The hydrogen peroxide thus generated would react with **8** to yield the epoxide **9**. The compound **8c** reacted readily with methanol at room temperature to give **10c**. Therefore, the enedione **8** probably reacts in an alcoholic solvent to give **10** or **11**. The hydroperoxy ketones **7** and **13** probably arise from different perepoxide intermediates.[12] Since hydroxy and carbonyl groups in the starting enol **6** should be *cis* owing to hydrogen bonding, two possible perepoxide intermediates may intervene, namely the form **A** and the form **B** (Scheme 4). Both perepoxides **A** and **B** would be expected to open to a stabilized benzilic cation **C**, which after proton shift gives **7**. The perepoxide **B** in which the terminal oxygen atom orients towards the methyl and aryl side would be also expected to be transformed into the hydroperoxide **13** by a hydrogen shift from the methyl group to the negative oxygen. Fukui has suggested by MO calculation that the terminal oxygen atom in the perepoxide from vinyl alcohol and singlet oxygen orients towards the hydroxy side.[13] He has also suggested that the perepoxide from aryl alkene and singlet oxygen has its terminal oxygen atom orientated towards the aromatic side. The regioselective $^1O_2$ ene reaction of alkoxy alkenes[14] and aryl alkenes[5,14] matches the expected geometry of the perepoxide intermediate. Since the enols **6** have hydroxy and aryl groups on C-1, both **A** and **B** must intervene. Recently, Adam *et al.*[15] have reported that the singlet oxygenation of chiral allylic alcohols proceeded with a high degree of regio- and diastereo-selectivity, and explained this selectivity in terms of coordination of the hydroxy functionality with the incoming $^1O_2$. They suggested that the reaction of allylic alcohols with singlet oxygen proceeds by an initial interaction of the nucleophilic oxygen atom of these substrates with the electrophilic singlet oxygen, and that the negatively charged terminal oxygen atom of the subsequently formed perepoxide interacts with the hydroxy group through hydrogen bonding. In the perepoxide **A**, the hydroxy group can interact with the terminal oxygen through hydrogen bonding by way of a five-membered ring. The reaction of singlet oxygen with α,β-unsaturated carbonyl compounds generally shows geminal selectivity.[2–5] The products expected by the geminal selectivity in the reaction of the enols **6** and singlet oxygen are **8**, **9**, **10** and **11**. The formation of **7** may be attributed to the hydrogen bonding in the perepoxide intermediate **A**.



Scheme 4 *Conditions*: i, $^1O_2$; ii, loss of H_2O_2; iii, R′OH; iv, H_2O_2

As seen from Table 1, the yield of the epoxide **9** was higher with $R^1 = Me$ than with $R^1 = Pr^i$ and decreased with bulky R^2. This result may be ascribed to steric factors. As already stated, the epoxide **9** is probably formed by the reaction of the enedione **8** with hydrogen peroxide. The more crowded enediones **8a–c** would be less reactive to hydrogen peroxide than the less crowded **8d–f**. In **8d–f**, **8f** is most crowded and therefore least reactive. In the reaction of **6d–f** in acetonitrile, the yield of the hydroperoxy ketone **7** was dependent on R^2. The yield decreased in the order of **7f**, **7e** and **7d**, while the total yield of **8** and **9** was the same regardless of R^2. Of the compounds **7d–f**, **7d** is the least crowded and probably most unstable because of its relative freedom from steric protection. The lower yield of **7d** compared with those of **7e** and **7f** is probably ascribed to partial decomposition during the isolation procedure.

The hydroperoxy ketone **7** with the same substituents was formed in slightly higher yield in acetonitrile than in methanol, while the total yield of the products arising from the perepoxide **B** (**8** and **9** in acetonitrile; **9** and **10** in methanol) was lower in acetonitrile than in methanol. The solvent effect on the singlet oxygenation of allylic alcohols has been reported.[12*i*,15*b*] The hydrogen bonding between the solvent and the hydroxy group

Table 1 Product distribution of the Methylene Blue-sensitized photooxidation of **6**[a]

Compound **6**	Solvent	Conversion (%)[b]	Yield(%)[c]				
			7	**8**	**9**	**10**	**11**
a	MeCN	97	35	42	6	—	—
b	MeCN	91	37	51	—	—	—
c	MeCN	100	36	55	—	—	—
d	MeCN	100	18	27	16	—	—
e	MeCN	95	28	31	10	—	—
f	MeCN	100	32	37	7	—	—
a	MeOH	91	23	—	6	61	—
a	EtOH	93	15	—	10	—	72
b	MeOH	94	33	—	3	59	—
c	MeOH	100	37	—	—	52	—
e	MeOH	94	25	—	6	40	—
f	MeOH	100	27	—	7	47	—

[a] A solution of **6** (500 mg) in a solvent (100 cm^3) in the presence of Methylene Blue (*ca.* 10 mg) was irradiated with a 100 W tungsten–halogen lamp through a K_2CrO_4 filter solution. [b] Based on the amount of unchanged starting material recovered after chromatography. [c] Based on converted starting material.

in a perepoxide intermediate affects product distribution. The internal hydrogen bond in the perepoxide **A** would be lessened in polar solvents. Hence, structure **A** should become less decisive relative to **B** and the yield of **7** should decrease. Methanol is slightly more effective than acetonitrile.[12i]

Experimental

Mps are uncorrected and bps are oven temperatures in Kugelrohr distillation. IR spectra were recorded on a Hitachi 270-50 spectrometer for solutions in CCl_4. ^1H NMR spectra were obtained with a Bruker AC 200 or a Bruker AM 400 spectrometer with $CDCl_3$ as a solvent. Tetramethylsilane was used as an internal standard and *J* values are given in Hz. ^{13}C NMR spectra were measured on a Bruker AC 200 or a Bruker AM 400 spectrometer with $CDCl_3$ as a solvent. Column chromatography was performed with Merck Kieselgel 60. A 100 W tungsten–halogen lamp was used as an irradiation source. Starting compounds **6a**–**f** were prepared by previously reported methods.[10]

General procedure for the photooxidation of 6

A solution of **6** (500 mg) in acetonitrile, methanol or ethanol (100 cm^3) through which air was bubbled in the presence of Methylene Blue (10–15 mg) was irradiated with a 100 W tungsten–halogen lamp through an aqueous solution of K_2CrO_4 (0.27 g dm^{-3}) and Na_2CO_3 (2 g dm^{-3}) for 3–15 h. The mixture was then evaporated under reduced pressure, and the residue was chromatographed on silica gel [hexane–ethyl acetate (8 : 1 to 12 : 1)] to give compounds **7**–**11**.

2-Hydroperoxy-1-(2′,4′,6′-triisopropylphenyl)-2-methylbutane-1,3-dione 7a. Mp 87–88 °C (from pentane) (Found: C, 71.9; H, 9.1. $C_{20}H_{30}O_4$ requires C, 71.8; H, 9.0%); ν_{max}/cm^{-1} 3450br (OOH), 1740 (C=O) and 1700 (C=O); δ_H(400 MHz) 1.10 (3 H, d, *J* 7), 1.14 (3 H, d, *J* 7), 1.19 (3 H, d, *J* 7) and 1.32 (3 H, d, *J* 7) (2′-CH*Me*$_2$ and 6′-CH*Me*$_2$), 1.24 (6 H, d, *J* 7, 4′-CH*Me*$_2$), 1.80 (3 H, s, 2-Me), 2.36 (1 H, sept. *J* 7), 2.54 (1 H, sept, *J* 7) and 2.88 (1 H, sept, *J* 7) (3 × C*H*Me$_2$), 2.41 (3 H, s, 4-H$_3$), 6.99 (1 H, s) and 7.00 (1 H, s) (ArH) and 8.90 (1 H, s, OOH); δ_C(100 MHz) 20.8 (q), 23.0 (q), 23.1 (q), 23.8 (2q), 25.2 (2q) and 25.7 (q) (C-4, 2-Me and 3 × CH*Me*$_2$), 31.5 (d), 32.2 (d) and 34.2 (d) (3 × *C*HMe$_2$), 98.7 (s, C-2), 121.1 (d), 121.3 (d), 134.1 (s), 144.8 (s), 144.9 (s) and 150.4 (s) (ArC), 204.2 (s) and 205.9 (s) (2 × C=O).

2-Hydroperoxy-1-(2′,4′,6′-triisopropylphenyl)-2-methylpentane-1,3-dione 7b. Mp 74–75 °C (from pentane) (Found: C, 72.5; H, 9.1. $C_{21}H_{32}O_4$ requires C, 72.4; H, 9.3%); ν_{max}/cm^{-1} 3460br (OOH), 1730 (C=O) and 1700 (C=O); δ_H(400 MHz) 1.09 (3 H, d, *J* 7), 1.13 (3 H, d, *J* 7), 1.18 (3 H, d, *J* 7) and 1.32 (3 H, d, *J* 7) (2′-CH*Me*$_2$ and 6′-CH*Me*$_2$), 1.10 (3 H, t, *J* 7, 5-H$_3$), 1.24 (6 H, d, *J* 7, 4′-CH*Me*$_2$), 1.81 (3 H, s, 2-Me), 2.29 (1 H, sept, *J* 7), 2.52 (1 H, sept, *J* 7) and 2.86 (1 H, sept, *J* 7) (3 × C*H*Me$_2$), 2.71 (1 H, dq, *J* 19 and 7) and 2.92 (1 H, dq, *J* 19 and 7) (4-H$_2$), 6.98 (1 H, s) and 7.00 (1 H, s) (ArH) and 8.94 (1 H, s, OOH); δ_C(100 MHz) 7.7 (q), 20.9 (q), 23.0 (q), 23.1 (q), 23.8 (2q), 25.2 (2q) (C-5, 2-Me and 3 × CH*Me*$_2$), 30.8 (t, C-4), 31.5 (d), 32.3 (d) and 34.2 (d) (3 × *C*HMe$_2$), 98.9 (s, C-2), 121.1 (d), 121.2 (d), 134.1 (s), 144.7 (s), 144.8 (s) and 150.3 (s) (ArC), 206.0 (s) and 206.9 (s) (2 × C=O).

2-Hydroperoxy-1-(2′,4′,6′-triisopropylphenyl)-2,4-dimethylpentane-1,3-dione 7c. Mp 100–102 °C (from pentane) (Found: C, 72.8; H, 9.5. $C_{22}H_{34}O_4$ requires C, 72.9; H, 9.5%); ν_{max}/cm^{-1} 3460br (OOH), 1740 (C=O) and 1700 (C=O); δ_H(400 MHz) 1.08 (3 H, d, *J* 7), 1.13 (3 H, d, *J* 7), 1.15 (3 H, d, *J* 7), 1.17 (3 H, d, *J* 7), 1.19 (3 H, d, *J* 7), 1.24 (6 H, d, *J* 7) and 1.31 (3 H, d, *J* 7) (5-H$_3$, 4-Me and 3 × CH*Me*$_2$), 1.81 (3 H, s, 2-Me), 2.41 (1 H, sept, *J* 7), 2.57 (1 H, sept, *J* 7), 2.88 (1 H, sept, *J* 7) and 3.52 (1 H, sept, *J* 7) (3 × ArC*H*Me$_2$ and 4-H), 6.98 (1 H, s) and 7.01 (1 H, s) (ArH) and 8.89 (1 H, s, OOH); δ_C(100 MHz) 20.1 (2q), 20.8 (q), 22.9 (q), 23.2 (q), 23.8 (2q), 25.1 (2q) (C-5, 4-Me, 2-Me and 3 × CH*Me*$_2$), 31.4 (d), 32.1 (d), 34.2 (d) and 35.4 (d) (4 × CH*Me*$_2$), 98.6 (s, C-2), 121.1 (d) and 121.3 (d), 134.5 (s), 144.8 (s), 145.0 (s) and 150.4 (s) (ArC), 206.4 (s) and 211.4 (s) (2 × C=O).

2-Hydroperoxy-2-methyl-1-(2′,4′,6′-trimethylphenyl)butane-1,3-dione 7d.† ν_{max}/cm^{-1} 3480br (OOH), 1740 (C=O) and 1700 (C=O); δ_H(200 MHz) 1.78 (3 H, s, 2-Me), 2.13 (6 H, s), 2.27 (3 H, s) and 2.40 (3 H, s) (3 × ArMe and 4-H$_3$), 6.82 (2 H, s, ArH) and 8.95 (1 H, s, OOH); δ_C(50 MHz) 19.7 (2q), 20.2 (q), 20.9 (q) and 25.6 (q) (5 × Me), 98.2 (s, C-2), 128.4 (2d), 133.5 (2s), 136.5 (s) and 139.0 (s) (ArC), 204.1 (s) and 205.6 (s) (2 × C=O).

2-Hydroperoxy-2-methyl-1-(2′,4′,6′-trimethylphenyl)pentane-1,3-dione 7e. Mp 74–75 °C (from pentane) (Found: C, 68.1; H, 7.7. $C_{15}H_{20}O_4$ requires C, 68.2; H, 7.6%); ν_{max}/cm^{-1} 3460br (OOH), 1740 (C=O) and 1700 (C=O); δ_H(200 MHz) 1.08 (3 H, t, *J* 7, 5-H$_3$), 1.76 (3 H, s, 2-Me), 2.10 (6 H, s) and 2.26 (3 H, s) (3 × ArMe), 2.6–3.0 (2 H, m, 4-H$_2$), 6.80 (2 H, s, ArH) and 9.13 (1 H, s, OOH); δ_C(50 MHz) 7.4 (q, C-5), 19.7 (2q), 20.4 (q) and 20.9 (q) (3 × ArMe and 2-Me), 30.9 (t, C-4), 98.3 (s, C-2), 128.4 (2d), 133.4 (2s), 136.4 (s) and 138.9 (s) (ArC), 205.8 (s) and 206.8 (s) (2 × C=O).

2-Hydroperoxy-2,4-dimethyl-1-(2′,4′,6′-trimethylphenyl)-pentane-1,3-dione 7f. Mp 64–65 °C (from pentane) (Found: C, 68.8; H, 8.0. $C_{16}H_{22}O_4$ requires C, 69.0; H, 8.0%); ν_{max}/cm^{-1} 3460br (OOH), 1740 (C=O) and 1700 (C=O); δ_H(200 MHz) 1.14 (3 H, d, *J* 7) and 1.17 (3 H, d, *J* 7) (5-H$_3$ and 4-Me), 1.81 (3 H, s, 2-Me), 2.15 (6 H, s) and 2.27 (3 H, s) (3 × ArMe), 3.48 (1 H,

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† Compounds **7d**, **8d**–**f** and **12d** were obtained as oils which decomposed on distillation.

sept, *J* 7, 4-H), 6.83 (2 H, s, ArH) and 8.89 (1 H, s, OOH); δ_C(50 MHz) 20.0 (2q), 20.2 (2q), 20.7 (q) and 21.0 (q) (6 × Me), 35.5 (d, C-4), 98.2 (s, C-2), 128.6 (2d), 133.7 (2s), 136.8 (s) and 139.1 (s) (ArC), 206.2 (s) and 211.0 (s) (2 × C=O).

1-(2′,4′,6′-Triisopropylphenyl)-2-methylenebutane-1,3-dione 8a. Mp 71–73 °C (from pentane) (Found: C, 79.9; H, 9.5. $C_{20}H_{28}O_2$ requires C, 80.0; H, 9.4%); ν_{max}/cm^{-1} 1720 (C=O) and 1690 (C=O); δ_H(400 MHz) 1.19 (12 H, d, *J* 7) and 1.26 (6 H, d, *J* 7) (3 × CH*Me*$_2$), 2.55 (3 H, s, 4-H$_3$), 2.68 (2 H, sept, *J* 7) and 2.70 (1 H, sept, *J* 7) (3 × C*H*Me$_2$), 5.92 (1 H, s) and 6.60 (1 H, s) (AB-pair, =CH$_2$) and 7.02 (2 H, s) (ArH); δ_C(100 MHz) 23.9 (2q), 24.1 (4q) and 30.2 (q) (3 × CH*Me*$_2$ and C-4), 31.0 (2d) and 34.3 (d) (3 × *C*HMe$_2$), 121.1 (2d), 134.0 (s), 145.0 (2s), 150.3 (s) and 150.5 (s) (ArC and C-2), 135.6 (t, =CH$_2$), 199.0 (s) and 200.4 (s) (2 × C=O).

1-(2′,4′,6′-Triisopropylphenyl)-2-methylenepentane-1,3-dione 8b. Mp 70–71 °C (from pentane) (Found: C, 80.0; H, 9.7. $C_{21}H_{30}O_2$ requires C, 80.2; H, 9.6%); ν_{max}/cm^{-1} 1700 (C=O) and 1670 (C=O); δ_H(400 MHz) 1.17 (3 H, t, *J* 7, 5-H$_3$), 1.18 (12 H, d, *J* 7) and 1.26 (6 H, d, *J* 7) (3 × CH*Me*$_2$), 2.69 (2 H, sept, *J* 7) and 2.90 (1 H, d, *J* 7) (3 × C*H*Me$_2$), 2.92 (2 H, q, *J* 7, 4-H$_2$), 5.89 (1 H, s) and 6.52 (1 H, s) (AB-pair, =CH$_2$) and 7.01 (2 H, s, ArH); δ_C(100 MHz) 7.7 (q), 23.9 (2q) and 24.1 (4q) (C-5 and 3 × CH*Me*$_2$), 31.5 (2d) and 34.3 (d) (3 × *C*HMe$_2$), 36.0 (t, C-4), 121.0 (2d), 134.0 (s), 145.0 (2s), 150.2 (s) and 150.9 (s) (ArC and C-2), 134.8 (t, =CH$_2$), 200.5 (s) and 202.5 (s) (2 × C=O).

1-(2′,4′,6′-Triisopropylphenyl)-2-methylene-4-methylpentane-1,3-dione 8c. Mp 71–72 °C (from pentane) (Found: C, 80.7; H, 9.8. $C_{22}H_{32}O_2$ requires C, 80.4; H, 9.8%); ν_{max}/cm^{-1} 1700 (C=O) and 1670 (C=O); δ_H(400 MHz) 1.18 (18 H, d, *J* 7) and 1.26 (6 H, d, *J* 7) (5-H$_3$, 4-Me and 3 × CH*Me*$_2$), 2.72 (2 H, sept, *J* 7), 2.90 (1 H, sept, *J* 7) and 3.27 (1 H, sept, *J* 7) (3 × C*H*Me$_2$ and 4-H), 5.87 (1 H, s) and 6.37 (1 H, s) (AB-pair, =CH$_2$) and 7.02 (2 H, s, ArH); δ_C(100 MHz) 18.0 (2q), 23.9 (2q) and 24.1 (4q) (C-5, 4-Me and 3 × CH*Me*$_2$), 31.0 (2d), 34.3 (d) and 39.7 (d) (4 × *C*HMe$_2$), 121.0 (2d), 133.8 (s + t), 145.1 (2s), 150.2 (s) and 151.3 (s) (ArC, C-2 and =CH$_2$), 200.4 (s) and 207.0 (s) (2 × C=O).

2-Methylene-1-(2′,4′,6′-trimethylphenyl)butane-1,3-dione 8d.† ν_{max}/cm^{-1} 1705 (C=O) and 1680 (C=O); δ_H(200 MHz) 2.17 (6 H, s), 2.25 (3 H, s) and 2.30 (3 H, s) (3 × ArMe and 4-H$_3$), 5.90 (1 H, s) and 6.56 (1 H, s) (AB-pair, =CH$_2$) and 6.86 (2 H, s, ArH); δ_C(50 MHz) 19.2 (2q), 21.0 (q) and 29.9 (q) (4 × Me), 128.5 (2d), 134.8 (2s), 136.0 (s), 139.1 (s) and 149.5 (s) (ArC and C-2), 134.1 (t, =CH$_2$), 198.5 (s) and 199.8 (s) (2 × C=O).

2-Methylene-1-(2′,4′,6′-trimethylphenyl)pentane-1,3-dione 8e.† ν_{max}/cm^{-1} 1710 (C=O) and 1680 (C=O); δ_H(200 MHz) 1.16 (3 H, t, *J* 7, 5-H$_3$), 2.17 (6 H, s) and 2.29 (3 H, s) (3 × ArMe), 2.87 (2 H, q, *J* 7, 4-H$_2$), 5.88 (1 H, s) and 6.49 (1 H, s) (AB-pair, =CH$_2$) and 6.85 (2 H, s, ArH); δ_C(50 MHz) 7.6 (q, C-5), 19.1 (2q) and 20.9 (q) (3 × ArMe), 35.5 (t, C-4), 128.4 (2d), 134.0 (2s + t), 136.0 (s), 138.9 (s) and 149.7 (s) (ArC, C-2 and =CH$_2$), 199.8 (s) and 201.9 (s) (2 × C=O).

4-Methyl-2-methylene-1-(2′,4′,6′-trimethylphenyl)pentane-1,3-dione 8f.† ν_{max}/cm^{-1} 1720 (C=O) and 1680 (C=O); δ_H(200 MHz) 1.18 (6 H, d, *J* 7, 5-H$_3$ and 4-Me), 2.18 (6 H, s) and 2.29 (3 H, s) (3 × ArMe), 3.26 (1 H, sept, *J* 7, 4-H), 5.89 (1 H, s) and 6.36 (1 H, s) (AB-pair, =CH$_2$) and 6.86 (2 H, s, ArH); δ_C(50 MHz) 18.0 (2q), 19.2 (2q) and 21.0 (q) (C-5, 4-Me and 3 × ArMe), 39.5 (d, C-4), 128.4 (2d), 134.2 (2s), 135.8 (s), 139.0 (s) and 149.5 (s) (ArC and C-2), 133.5 (t, =CH$_2$), 199.8 (s) and 206.6 (s) (2 × C=O).

3,4-Epoxy-3-(2′,4′,6′-triisopropylbenzoyl)butan-2-one 9a. Mp 78–79 °C (from pentane) (Found: C, 75.8; H, 9.0. $C_{20}H_{28}O_3$ requires C, 75.9; H, 8.9%); ν_{max}/cm^{-1} 1730 (C=O) and 1700 (C=O); δ_H(200 MHz) 1.20 (6 H, d, *J* 7), 1.24 (6 H, d, *J* 7) and 1.25 (6 H, d, *J* 7) (3 × CH*Me*$_2$), 2.40 (3 H, s, 1-H$_3$), 2.70 (2 H, sept, *J* 7) and 2.88 (1 H, sept, *J* 7) (3 × C*H*Me$_2$), 2.99 (1 H, d, *J* 6) and 3.11 (1 H, d, *J* 6) (4-H$_2$) and 6.99 (2 H, s) (ArH); δ_C(50 MHz) 23.8 (2q), 24.0 (2q), 24.4 (2q) and 27.8 (q) (3 × CH*Me*$_2$ and C-1), 31.5 (2d) and 34.3 (d) (3 × *C*HMe$_2$), 51.5 (t, C-4), 64.2 (s, C-3), 120.9 (2d), 131.1 (s), 145.7 (2s), 150.8 (s) (ArC), 200.7 (s) and 204.0 (s) (2 × C=O).

1,2-Epoxy-2-(2′,4′,6′-triisopropylbenzoyl)pentan-3-one 9b. Mp 75–76 °C (from pentane) (Found: C, 76.4; H, 9.1. $C_{21}H_{30}O_3$ requires C, 76.3; H, 9.2%); ν_{max}/cm^{-1} 1730 (C=O) and 1690 (C=O); δ_H(200 MHz) 1.13 (3 H, t, *J* 7, 5-H$_3$), 1.20 (6 H, d, *J* 7), 1.24 (6 H, d, *J* 7) and 1.25 (6 H, d, *J* 7) (3 × CH*Me*$_2$), 2.71 (2 H, sept, *J* 7) and 2.88 (1 H, sept, *J* 7) (3 × C*H*Me$_2$), 2.74 (2 H, q, *J* 7, 4-H$_2$), 2.98 (1 H, d, *J* 6) and 3.08 (1 H, d, *J* 6) (1-H$_2$) and 6.99 (2 H, s, ArH); δ_C(50 MHz) 7.0 (q, C-5), 23.8 (2q), 24.0 (2q) and 24.4 (2q) (3 × CH*Me*$_2$), 31.5 (2d) and 34.3 (d) (3 × *C*HMe$_2$), 33.5 (t, C-4), 51.4 (t, C-1), 64.1 (s, C-2), 120.8 (2d), 131.1 (s), 145.7 (2s) and 150.7 (s) (ArC), 203.6 (s) and 204.3 (s) (2 × C=O).

3,4-Epoxy-3-(2′,4′,6′-trimethylbenzoyl)butan-2-one 9d. Bp 95 °C at 0.5 mmHg (Found: C, 72.3; H, 7.0. $C_{14}H_{16}O_3$ requires C, 72.4; H, 6.9%); ν_{max}/cm^{-1} 1730 (C=O) and 1700 (C=O); δ_H(200 MHz) 2.23 (6 H, s), 2.27 (3 H, s) and 2.39 (3 H, s) (3 × ArMe and 1-H$_3$), 2.97 (1 H, d, *J* 6) and 3.15 (1 H, d, *J* 6) (4-H$_2$) and 6.83 (2 H, s, ArH); δ_C(50 MHz) 19.1 (2q), 21.0 (q) and 27.3 (q) (3 × ArMe and C-1), 51.7 (t, C-4), 63.7 (s, C-3), 128.4 (2d), 133.1 (s), 134.8 (2s) and 139.7 (s) (ArC), 200.4 (s) and 202.8 (s) (2 × C=O).

1,2-Epoxy-2-(2′,4′,6′-trimethylbenzoyl)pentan-3-one 9e. Bp 84 °C at 0.3 mmHg (Found: C, 73.3; H, 7.2. $C_{15}H_{18}O_3$ requires C, 73.2; H, 7.4%); ν_{max}/cm^{-1} 1730 (C=O) and 1700 (C=O); δ_H(200 MHz) 1.11 (3 H, t, *J* 7, 5-H$_3$), 2.22 (6 H, s) and 2.26 (3 H, s) (3 × ArMe), 2.72 (2 H, q, *J* 7, 4-H$_2$), 2.94 (1 H, d, *J* 6) and 3.12 (1 H, d, *J* 6) (1-H$_2$) and 6.82 (2 H, s, ArH); δ_C(50 MHz) 6.9 (q, C-5), 19.1 (2q) and 21.0 (q) (3 × ArMe), 33.1 (t, C-4), 51.6 (t, C-1), 63.7 (s, C-2), 128.3 (2d), 133.1 (s), 134.7 (2s) and 139.6 (s) (ArC) and 203.2 (2s) (2 × C=O).

1,2-Epoxy-4-methyl-2-(2′,4′,6′-trimethylbenzoyl)pentan-3-one 9f. Bp 118 °C at 0.5 mmHg (Found: C, 73.9; H, 7.7. $C_{16}H_{20}O_3$ requires C, 73.8; H, 7.7%); ν_{max}/cm^{-1} 1735 (C=O) and 1705 (C=O); δ_H(200 MHz) 1.12 (3 H, d, *J* 7) and 1.20 (3 H, d, *J* 7) (5-H$_3$ and 4-Me), 2.23 (6 H, s) and 2.27 (3 H, s) (3 × ArMe), 2.96 (1 H, d, *J* 6) and 3.05 (1 H, d, *J* 6) (1-H$_2$), 3.02 (1 H, sept, *J* 7, 4-H) and 6.82 (2 H, s, ArH); δ_C(50 MHz) 17.4 (q), 18.3 (q), 19.2 (2q) and 21.0 (q) (C-5, 4-Me and 3 × ArMe), 37.5 (d, C-4), 51.7 (t, C-1), 63.4 (s, C-2), 128.3 (2d), 133.2 (s), 134.8 (2s) and 139.6 (s) (ArC), 203.1 (s) and 206.9 (s) (2 × C=O).

1-(2′,4′,6′-Triisopropylphenyl)-2-methoxymethylbutane-1,3-dione 10a.‡ ν_{max}/cm^{-1} 1610 (C=O) and 1590 (C=C); δ_H(200 MHz) 1.18 (12 H, d, *J* 7) and 1.26 (6 H, d, *J* 7) (3 × CH*Me*$_2$), 2.32 (3 H, s, 4-H$_3$), 2.89 (3 H, sept, *J* 7, 3 × C*H*Me$_2$), 3.11 (3 H, s, OMe), 3.77 (2 H, s, C*H*$_2$OMe), 7.03 (2 H, s, ArH) and 16.61 (1 H, s, enolic OH); δ_C(50 MHz) 23.1 (2q), 23.8 (2q) and 25.1 (2q) (3 × CH*Me*$_2$), 24.5 (q, C-4), 30.7 (2d) and 34.2 (d) (3 × *C*HMe$_2$), 57.6 (q, OMe), 68.9 (t, *C*H$_2$OMe), 110.8 (s, C-2), 120.5 (2d), 130.2 (s), 145.0 (2s) and 149.7 (s) (ArC), 186.8 (s, C-1) and 199.2 (s, C-3).

2-Ethoxymethyl-1-(2′,4′,6′-triisopropylphenyl)butane-1,3-dione 11a.‡ ν_{max}/cm^{-1} 1610 (C=O) and 1590 (C=C); δ_H(400 MHz) 1.09 (3 H, t, *J* 7, OCH$_2$*Me*), 1.17 (6 H, d, *J* 7), 1.18 (6 H, d, *J* 7) and 1.26 (6 H, d, *J* 7) (3 × CH*Me*$_2$), 2.36 (3 H, s, 4-H$_3$), 2.90 (3 H, sept, *J* 7, 3 × C*H*Me$_2$), 3.27 (2 H, q, *J* 7, OC*H*$_2$Me), 3.82 (2 H, s, C*H*$_2$OEt), 7.01 (2 H, s, ArH) and 16.75 (1 H, s, enolic OH); δ_C(100 MHz) 14.9 (q), 23.3 (2q), 23.9 (2q), 24.9 (q) and 25.2 (2q) (C-4, OCH$_2$*Me* and 3 × CH*Me*$_2$), 30.8 (2d) and 34.3 (d) (3 × *C*HMe$_2$), 65.6 (t) and 67.1 (t) (*C*H$_2$O*C*H$_2$Me), 111.0 (s, C-2), 120.7 (2d), 130.3 (s), 145.2 (2s) and 149.8 (s) (ArC), 186.3 (s, C-1) and 199.9 (s, C-3).

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‡ Compounds **10a**–**c**,**e** and **11a** were obtained as oils. These compounds underwent quantitative elimination of methanol (for **10**) or ethanol (for **11**) on distillation to give **8**.

1-(2′,4′,6′-Triisopropylphenyl)-2-methoxymethylpentane-1,3-dione 10b.‡ ν_{max}/cm^{-1} 1610 (C=O) and 1590 (C=C); δ_H(400 MHz) 1.67 (6 H, d, *J* 7), 1.18 (6 H, d, *J* 7) and 1.26 (6 H, d, *J* 7) (3 × $CHMe_2$), 1.20 (3 H, t, *J* 7, 5-H_3), 2.72 (2 H, q, *J* 7, 4-H_2), 2.85–2.95 (3 H, m, 3 × $CHMe_2$), 3.13 (3 H, s, OMe), 3.78 (2 H, s, CH_2OMe), 7.01 (2 H, s, ArH) and 16.68 (1 H, s, enolic OH); δ_C(50 MHz) 8.4 (q, C-5), 23.2 (2q), 23.9 (2q) and 25.2 (2q) (3 × $CHMe_2$), 30.3 (t, C-4), 30.8 (2d) and 34.3 (d) (3 × $CHMe_2$), 57.7 (q, OMe), 68.7 (t, CH_2OMe), 110.4 (s, C-2), 120.7 (2d), 130.1 (s), 145.3 (2s) and 149.8 (s) (ArC), 184.8 (s, C-1) and 203.5 (s, C-3).

1-(2′,4′,6′-Triisopropylphenyl)-2-methoxymethyl-4-methylpentane-1,3-dione 10c.‡ ν_{max}/cm^{-1} 1620 (C=O) and 1580 (C=C); δ_H(400 MHz) 1.17 (6 H, d, *J* 7), 1.18 (6 H, d, *J* 7), 1.21 (6 H, d, *J* 7) and 1.26 (6 H, d, *J* 7) (4 × $CHMe_2$), 2.88 (2 H, sept, *J* 7) and 3.05 (2 H, sept, *J* 7) (4 × $CHMe_2$), 3.08 (3 H, s, OMe), 3.78 (2 H, s, CH_2OMe), 7.01 (2 H, s, ArH) and 16.87 (1 H, s, enolic OH); δ_C(50 MHz) 19.5 (2q), 23.2 (2q), 23.9 (2q) and 25.3 (2q) (4 × $CHMe_2$), 30.9 (2d), 33.8 (d) and 34.3 (d) (3 × $CHMe_2$ and C-4), 57.7 (q, OMe), 68.6 (t, CH_2OMe), 109.6 (s, C-2), 120.7 (2d), 130.7 (s), 145.1 (2s) and 149.8 (s) (ArC), 188.1 (s, C-1) and 205.8 (s, C-3).

2-Methoxymethyl-1-(2′,4′,6′-trimethylphenyl)pentane-1,3-dione 10e.‡ ν_{max}/cm^{-1} 1610 (C=O) and 1590 (C=C); δ_H(200 MHz) 1.19 (3 H, t, *J* 7, 5-H_3), 2.19 (6 H, s) and 2.28 (3 H, s) (3 × ArMe), 2.71 (2 H, q, *J* 7, 4-H_2), 3.10 (3 H, s, OMe), 3.79 (2 H, s, CH_2OMe), 6.85 (2 H, s, ArH) and 16.57 (1 H, s, enolic OH); δ_C(50 MHz) 8.3 (q, C-5), 19.0 (2q) and 21.0 (q) (3 × ArMe), 30.4 (t, C-4), 57.6 (q, OMe), 68.5 (t, CH_2OMe), 109.4 (s, C-2), 127.9 (2d), 131.9 (s), 134.5 (2s) and 138.4 (s) (ArC), 183.9 (s, C-1) and 204.2 (s, C-3).

2-Methoxymethyl-4-methyl-1-(2′,4′,6′-trimethylphenyl)-pentane-1,3-dione 10f. Mp 58–59 °C (from pentane) (Found: C, 74.1; H, 8.8. $C_{17}H_{24}O_3$ requires C, 73.9; H, 8.8%); ν_{max}/cm^{-1} 1620 (C=O) and 1580 (C=C); δ_H(200 MHz) 1.20 (6 H, d, *J* 7, 5-H_3 and 4-Me), 2.19 (6 H, s) and 2.26 (3 H, s) (3 × ArMe), 3.06 (3 H, s, OMe), 3.07 (1 H, sept, *J* 7, 4-H), 3.80 (2 H, s, CH_2OMe), 6.84 (2 H, s, ArH) and 17.04 (1 H, s, enolic OH); δ_C(50 MHz) 18.9 (2q), 19.3 (2q) and 20.9 (q) (C-5, 4-Me and 3 × ArMe), 33.7 (d, C-4), 57.4 (q, OMe), 68.2 (t, CH_2OMe), 108.6 (s, C-2), 127.8 (2d), 132.5 (s), 134.2 (2s) and 138.2 (s) (ArC), 187.4 (s, C-1) and 206.3 (s, C-3).

General procedure for the deoxygenation of the hydroperoxides 7a,c–e

A mixture of the hydroperoxy compound **7a**,**c**–**e** (100–200 mg) and triphenylphosphine (1.1 equiv.) in benzene (15–30 cm^3) was stirred overnight at room temperature. Concentration under reduced pressure and subsequent chromatography on silica gel [hexane–ethyl acetate (15:1)] gave the hydroxy compounds **12a**,**c**–**e**.

2-Hydroxy-1-(2′,4′,6′-triisopropylphenyl)-2-methylbutane-1,3-dione 12a. Mp 72–73 °C (from pentane) (Found: C, 75.5; H, 9.5. $C_{20}H_{30}O_3$ requires C, 75.4; H, 9.5%); ν_{max}/cm^{-1} 3460br (OH), 1720 (C=O) and 1700 (C=O); δ_H(200 MHz) 1.09 (3 H, d, *J* 7), 1.12 (3 H, d, *J* 7), 1.16 (3 H, d, *J* 7) and 1.33 (3 H, d, *J* 7) (2′-$CHMe_2$ and 6′-$CHMe_2$), 1.24 (6 H, d, *J* 7, 4′-$CHMe_2$), 1.74 (3 H, s, 2-Me), 1.95 (1 H, sept, *J* 7), 2.61 (1 H, sept, *J* 7) and 2.87 (1 H, sept, *J* 7) (3 × $CHMe_2$), 2.47 (3 H, s, 4-H_3), 4.43 (1 H, s, OH), 6.94 (1 H, s) and 7.00 (1 H, s) (ArH); δ_C(50 MHz) 23.2 (2q), 23.6 (q), 23.8 (2q), 25.0 (q) and 25.1 (2q) (C-4, 2-Me and 3 × $CHMe_2$), 31.7 (d), 32.5 (d) and 34.2 (d) (3 × $CHMe_2$), 89.3 (s, C-2), 120.7 (d), 120.9 (d), 134.4 (s), 143.6 (s), 145.4 (s) and 149.7 (s) (ArC), 205.5 (s) and 212.3 (s) (2 × C=O).

2-Hydroxy-1-(2′,4′,6′-triisopropylphenyl)-2,4-dimethylpentane-1,3-dione 12c. Mp 73–74 °C (from hexane) (Found: C, 76.3; H, 10.0. $C_{24}H_{34}O_3$ requires C, 76.3; H, 9.9%); ν_{max}/cm^{-1} 3460br (OH), 1710 (C=O) and 1695 (C=O); δ_H(200 MHz) 1.05 (3 H, d, *J* 7), 1.12 (3 H, d, *J* 7), 1.15 (3 H, d, *J* 7), 1.19 (3 H, d, *J* 7), 1.12 (3 H, d, *J* 7), 1.24 (6 H, d, *J* 7) and 1.32 (3 H, d, *J* 7) (4 × $CHMe_2$), 1.78 (3 H, s, 2-Me), 1.98 (1 H, sept, *J* 7), 2.65 (1 H, sept, *J* 7), 2.87 (1 H, sept, *J* 7) and 3.73 (1 H, d, *J* 7) (3 × $ArCHMe_2$ and 4-H), 4.52 (1 H, s, OH), 6.94 (1 H, s) and 7.01 (1 H, s) (ArH); δ_C(50 MHz) 19.5 (q), 21.1 (q), 23.0 (q), 23.5 (q), 23.9 (2q), 24.9 (q), 25.1 (q) and 25.3 (q) (4 × $CHMe_2$ and 2-Me), 31.7 (d), 32.2 (d), 34.2 (d) and 34.5 (d) (4 × $CHMe_2$), 88.8 (s, C-2), 120.7 (d), 121.1 (d), 135.0 (s), 143.6 (s), 145.0 (s) and 149.6 (s) (ArC), 212.5 (s) and 212.9 (s) (2 × C=O).

2-Hydroxy-2-methyl-1-(2′,4′,6′-trimethylphenyl)butane-1,3-dione 12d.† ν_{max}/cm^{-1} 3450br (OH), 1720 (C=O) and 1700 (C=O); δ_H(200 MHz) 1.75 (3 H, s, 2-Me), 2.07 (6 H, br s), 2.26 (3 H, s) and 2.47 (3 H, s) (3 × ArMe and 4-H_3), 4.48 (1 H, s, OH) and 6.80 (2 H, s, ArH); δ_C(50 MHz) 19.5 (q), 20.9 (q), 23.6 (q) and 24.7 (2q) (5 × Me), 89.1 (s, C-2), 128.1 (2d), 133.0 (2s), 136.9 (s) and 138.4 (s) (ArC), 205.7 (s) and 211.6 (s) (2 × C=O).

2-Hydroxy-2-methyl-1-(2′,4′,6′-trimethylphenyl)pentane-1,3-dione 12e. Mp 45–46 °C (from pentane) (Found: C, 72.7; H, 8.2. $C_{15}H_{20}O_3$ requires C, 72.6; H, 8.1%); ν_{max}/cm^{-1} 3470br (OH), 1720 (C=O) and 1700 (C=O); δ_H(200 MHz) 1.12 (3 H, t, *J* 7, 5-H_3), 1.73 (3 H, s, 2-Me), 2.04 (6 H, br s) and 2.25 (3 H, s) (3 × ArMe), 2.73 (1 H, dq, *J* 18 and 7) and 3.03 (1 H, dq, *J* 18 and 7) (4-H_2), 4.55 (1 H, s, OH) and 6.79 (2 H, s, ArH); δ_C(50 MHz) 7.5 (q, C-5), 19.5 (q), 20.9 (q) and 24.7 (2q) (2-Me and 3 × ArMe), 29.1 (t, C-4), 88.9 (s, C-2), 128.1 (2d), 133.2 (2s), 136.9 (s) and 138.4 (s) (ArC), 208.6 (s) and 211.9 (s) (2 × C=O).

Reaction of compound 8c with methanol

Compound **8c** (4 mg) dissolved in methanol (3 cm^3) was allowed to stand at room temperature for 1 h after which the solvent was removed under reduced pressure. ^{1}H NMR analysis of the residue showed the quantitative formation of the adduct **10c**.

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