

Cycloaddition reactions of 2-oxo-2*H*-cyclohepta[*b*]furan derivatives with arylacetylenes and the di- π -methane rearrangement of homobarrelene derivatives

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2-Oxo-2*H*-cyclohepta[*b*]furan derivatives participate in [4 + 2]cycloaddition reactions with aryl acetylenes leading to homobarrelene derivatives and the latter undergo di- π -methane rearrangement resulting in complex carbocycles.

Introduction

The 2-oxo-2*H*-cyclohepta[*b*]furans **1a,b**, readily obtained by the reaction of 2-chlorotropone with diethyl malonate and ethyl acetoacetate respectively, can be viewed as electron-deficient heptafulvenes.^{1,2} These compounds can participate either as 8π or 4π systems in cycloadditions.³ The [8 + 2]cycloadditions of **1a,b** with enamines^{4–8} and enol ethers^{9–11} have been exploited in the synthesis of azulene derivatives. Recently, we have reported that the cycloaddition reactions of **1a,b** with acyclic dienes proceeded in an [8 + 2] manner, yielding novel bicyclo[5.3.0]decane systems.^{12,13} In their reaction with fulvenes both [8 + 2] and [4 + 2] cycloadducts were obtained,¹⁴ whereas the reaction with arylalkenes proceeded exclusively in [4 + 2] mode.^{13,15} In this context, it was of interest to study the cycloaddition of **1a** and **1b** with arylacetylenes. The results of our investigations concerned with the cycloadditions and the di- π -methane rearrangement of the resulting adducts are reported here.

Results and discussion

1. Cycloaddition reactions of 3-substituted 2-oxo-2*H*-cyclohepta[*b*]furan derivatives with arylacetylenes

The reactions of **1a,b** with arylacetylenes **2a–d** in dry toluene in a Schlenk tube (ST) at 140 °C afforded exclusively the [4 + 2] adducts **3a–g** in very good yields (Scheme 1, Table 1).

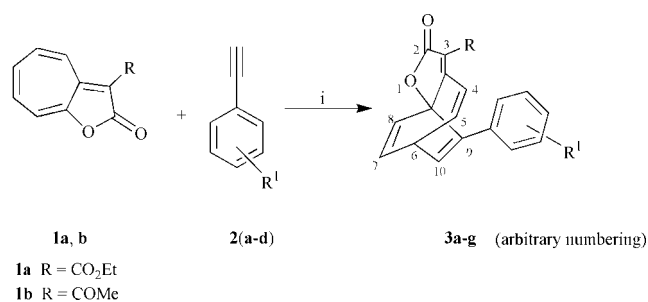
The structure of the products was ascertained on the basis of spectral and analytical data. For example, the IR spectrum of **3a** showed two carbonyl absorptions, at 1771 cm⁻¹ and 1710 cm⁻¹, corresponding to the lactone and ester carbonyl groups, respectively. In the ¹H NMR spectrum, the bridgehead proton resonated as a multiplet at δ 4.15 and the styrenic proton resonated as a doublet at δ 6.46. In the ¹³C NMR spectrum, the carbon adjacent to the oxygen atom appeared at δ_C 86.90 and the bridgehead carbon resonated at δ_C 41.19. The characteristic absorptions due to the lactone and ester carbonyls were visible at δ_C 168.25 and 162.32, respectively.

In an effort to rationalize the observed reactivity of **1a** and **1b** with arylacetylenes, we have carried out AM1 calculations using the PC SPARTAN Graphical Interface Package for Molecular Mechanics and Molecular Orbital Models. The results obtained using the reaction of **1a** with phenylacetylene **2a** as an example is illustrated in Fig. 1.

The exclusive formation of [4 + 2] adduct from **1a** and phenylacetylene can be explained in terms of the coefficients of the Frontier Orbitals at the reacting centers. It is clear from the correlation diagram that the interactions of HOMO(**1a**)–LUMO(**2a**), LUMO(**1a**)–HOMO(**2a**) and NLUMO(**1a**)–HOMO(**2a**) are symmetry allowed. The interaction of LUMO(**1a**)–HOMO(**2a**) is unimportant because of the small coefficients at C-2 and C-5 of LUMO(**1a**). The energy gap of NLUMO(**1a**)–HOMO(**2a**) is considerably smaller than that of HOMO(**1a**)–LUMO(**2a**). Therefore, the interaction of NLUMO(**1a**) with HOMO(**2a**) controls the [4 + 2]cycloaddition, which is a Diels–Alder reaction with inverse electron demand.

2. Photoisomerization of the homobarrelene derivatives

The products resulting from the cycloaddition of 2-oxo-2*H*-cyclohepta[*b*]furan derivatives **1a,b** and arylacetylenes **2** are



Scheme 1 Conditions: Δ , toluene, ST, 140 °C, 46 h.

Table 1

| Entry | Substituents | [4 + 2] adduct | Yield (%) ^a |
|-------|---|----------------|------------------------|
| 1 | R = CO ₂ Et, R ¹ = H | 3a | 90 |
| 2 | R = CO ₂ Et, R ¹ = Cl (<i>p</i>) | 3b | 71.5 |
| 3 | R = CO ₂ Et, R ¹ = OMe (<i>p</i>) | 3c | 66.4 |
| 4 | R = CO ₂ Et, R ¹ = CH ₃ (<i>p</i>) | 3d | 52 |
| 5 | R = COCH ₃ , R ¹ = H | 3e | 79 |
| 6 | R = COCH ₃ , R ¹ = Cl (<i>p</i>) | 3f | 63.7 |
| 7 | R = COCH ₃ , R ¹ = OMe (<i>p</i>) | 3g | 49 |

^a Yield based on unchanged **1a,b**.

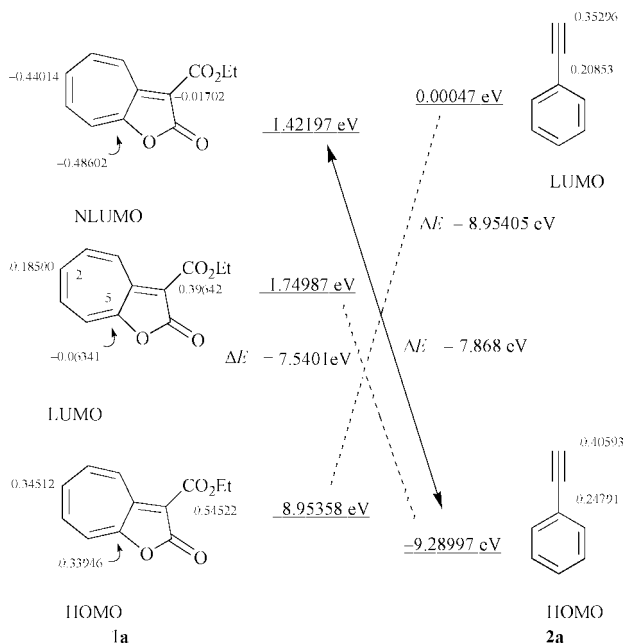
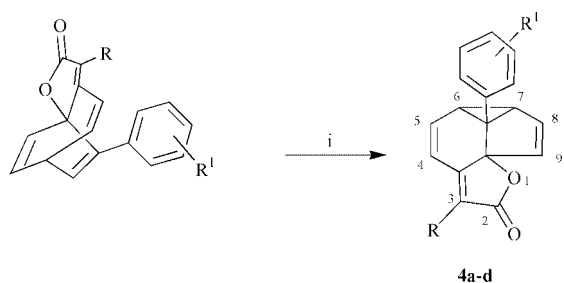


Fig. 1 Molecular orbital correlation diagrams of **1a** and phenylacetylene **2a**.

homobarrelenes and such systems are potentially amenable to di- π -methane rearrangement. Although the photoisomerization of barrelene derivatives has been studied in great detail,^{16,17} the photochemistry of homobarrelenes has received very little attention.¹⁸

A degassed solution of a [4 + 2] adduct in acetonitrile on irradiation at 300 nm in a Pyrex glass tube afforded the corresponding photoisomerized product **4a-d** in very good yield (Scheme 2, Table 2).

The structure of the products was assigned on the basis of spectral analysis. The IR spectrum of **4a** showed two carbonyl absorptions, at 1775 and 1715 cm^{-1} , characteristic of lactone and ester carbonyl groups, respectively. In the ^1H NMR spectrum, the protons on the cyclopropane ring resonated as multiplets at δ 3.25 and 2.59. In the ^{13}C NMR spectrum, the cyclopropane carbons were visible at δ_{C} 53.80, 48.90, and 35.57. The characteristic lactone and ester carbonyl groups were visible at δ_{C} 171.93 and δ_{C} 163.66, respectively. Finally, the structure of the product **4a** was confirmed by single-crystal X-ray analysis (Fig. 2).



Scheme 2 Conditions: i, CH_3CN , Pyrex, 300 nm.

Table 2

| Entry | Substituents | Reaction time | Product | Yield (%) ^a |
|-------|--|---------------|-----------|------------------------|
| 1 | R = CO_2Et , $\text{R}^1 = \text{H}$ | 1 h | 4a | 70 |
| 2 | R = CO_2Et , $\text{R}^1 = \text{Cl}$ (<i>p</i>) | 1 h | 4b | 78 |
| 3 | R = COCH_3 , $\text{R}^1 = \text{H}$ | 10 min | 4c | 80 |
| 4 | R = COCH_3 , $\text{R}^1 = \text{Cl}$ (<i>p</i>) | 10 min | 4d | 94 |

^a Isolated yield.

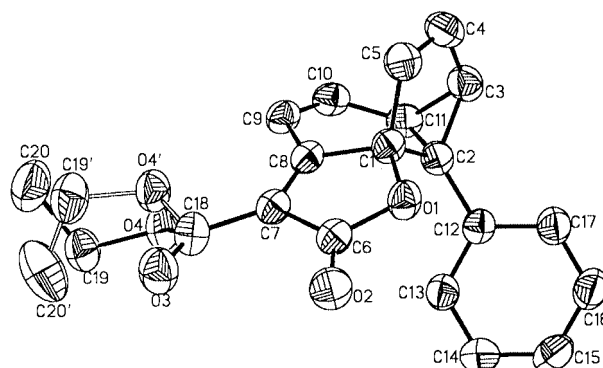
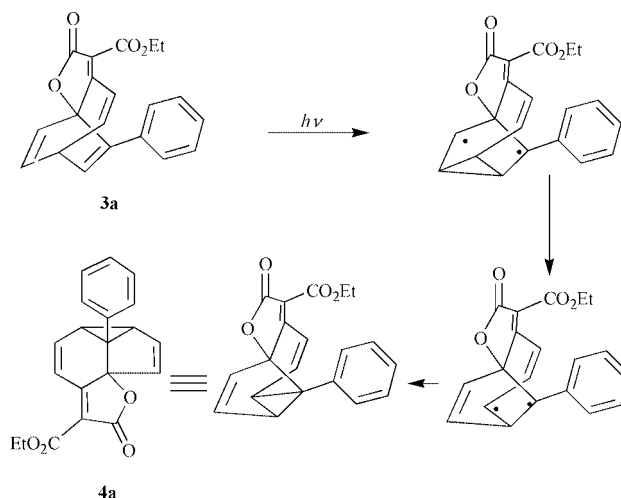


Fig. 2 X-Ray molecular structure of compound **4a**. Crystallographic numbering scheme shown.

In analogy with the di- π -methane rearrangement of barrelene derivatives, the following mechanistic rationale may be invoked for the photolytic rearrangement of **3a** (Scheme 3).



Scheme 3

In conclusion, we have observed a simple and exclusive [4 + 2]cycloaddition of **1a,b** with arylacetylenes leading to homobarrelene derivatives; the latter undergo di- π -methane rearrangement smoothly.

Experimental

All reactions were carried out in oven-dried glassware under argon atmosphere. Analytical TLC was performed on silica gel TLC plates. Purification by gravity column chromatography was carried out using silica gel (100–200). Mixtures of ethyl acetate–hexane and chloroform–methanol were used as eluents. All mps were measured on a Buchi-530 melting point apparatus and are uncorrected. IR spectra were recorded on a Nicolet impact 400D infrared spectrophotometer. NMR spectra were recorded on a Bruker 300 spectrophotometer using chloroform-*d* as solvent. Chemical shifts are given in the δ -scale with tetramethylsilane as internal standard.

Preparation of, and data for, **3a**

Ethyl 2-oxo-2H-cyclohepta[b]furan-3-carboxylate **1a** (0.218 g, 1 mmol) and phenylacetylene **2a** (0.306 g, 3 mmol) in dry toluene (1 mL) were sealed under argon in a Schlenk tube and heated at 140 $^\circ\text{C}$ for 46 h. The reaction mixture was chromatographed on a silica gel column (10% ethyl acetate–hexane) to afford the adduct **3a** (0.111 g, 90%) as a yellow semi-solid. The unchanged furanone (0.134 g) was recovered. Product **3a** (Found: C, 74.81; H, 4.78. $\text{C}_{20}\text{H}_{16}\text{O}_4$ requires C, 74.99; H,

5.03%); ν_{\max} (KBr)/ cm^{-1} 1771 (lactone), 1710 (ester); δ_{H} 7.27 (m, 3 H, ArH), 7.15 (m, 2 H, ArH), 6.99 (dd, J 10.5, 8.1, 1 H, 5-H), 6.88 (d, J 10.5, 1 H, 4-H), 6.72 (dd, J 7.8, 6.9, 1 H, 7-H), 6.56 (d, J 6.59, 1 H, 8-H), 6.46 (d, J 7.80, 1 H, 10-H), 4.33 (q, J 7.20, 2 H, OCH_2CH_3), 4.15 (m, 1 H, bridgehead), 1.35 (t, J 7.2, 3 H, OCH_2CH_3); δ_{C} 168.25, 162.32, 161.04, 146.03, 144.48, 134.52, 133.98, 133.09, 131.30, 128.49, 127.95, 127.89, 118.82, 112.17, 86.90, 61.18, 41.19, 13.95.

Preparation of, and data for, 3b

Reaction of **1a** (0.218 g, 1 mmol) and *p*-chlorophenylacetylene **2b** (0.273 g, 2 mmol), as described earlier for **3a**, yielded **3b** (0.136 g, 71.5%) as a yellow semi-solid. The unchanged furanone (0.101 g) was recovered. Product **3b** showed ν_{\max} (KBr)/ cm^{-1} 1782 (lactone), 1715 (ester); δ_{H} 7.21 (m, 2 H, ArH), 7.07 (m, 2 H, ArH), 6.98 (dd, J 10.56, 8.26, 1 H, 5-H), 6.87 (d, J 10.19, 1 H, 4-H), 6.72 (dd, J 7.48, 6.72, 1 H, 7-H), 6.57 (d, J 6.1, 1 H, 8-H), 6.42 (d, J 7.71, 1 H, 10-H), 4.34 (q, J 7.07, 2 H, OCH_2CH_3), 4.19 (m, 1 H, bridgehead), 1.35 (t, J 7.08, 3 H, OCH_2CH_3); δ_{C} 168.15, 162.22, 161.08, 146.14, 143.58, 134.18, 133.05, 132.07, 130.07, 128.35, 119.06, 112.41, 86.79, 61.43, 41.36, 14.15; m/z (HRMS) 354.066491 (M^+ , $\text{C}_{20}\text{H}_{15}\text{ClO}_4$ requires M , 354.065887).

Preparation of, and data for, 3c

Reaction of **1a** (0.15 g, 0.69 mmol) and *p*-methoxyphenylacetylene **2c** (0.182 g, 1.38 mmol), as described earlier for **3a**, yielded **3c** (0.097 g, 66.4%) as a semi-solid. The unchanged furanone (0.059 g) was recovered. Product **3c** showed ν_{\max} (KBr)/ cm^{-1} 1775 (lactone), 1715 (ester); δ_{H} 7.13 (m, 2 H, ArH), 6.96 (m, 2 H, ArH), 6.87–6.80 (m, 2 H, 4- and 5-H), 6.75 (dd, J 7.78, 7.73, 1 H, 7-H), 6.52 (d, J 6.62, 1 H, 8-H), 6.45 (d, J 7.02, 1 H, 10-H), 4.35 (q, J 7.04, 2 H, OCH_2CH_3), 4.14 (m, 1 H, bridgehead), 3.71 (s, 3 H, OCH_3), 1.36 (t, J 7.08, 3 H, OCH_2CH_3); δ_{C} 168.45, 162.68, 161.27, 159.58, 146.37, 144.28, 134.01, 133.21, 130.35, 130.05, 126.75, 119.02, 113.65, 112.27, 87.18, 61.38, 55.23, 41.37, 14.16; m/z (HRMS) 350.115759 (M^+ , $\text{C}_{21}\text{H}_{18}\text{O}_3$ requires M , 350.115424).

Preparation of, and data for, 3d

Reaction of **1a** (0.218 g, 1 mmol) and *p*-methylphenylacetylene **2d** (0.232 g, 2 mmol), as described earlier for **3a**, yielded **3d** (0.103 g, 52%) as a semi-solid. The unchanged furanone (0.088 g) was recovered. Product **3d** showed ν_{\max} (KBr)/ cm^{-1} 1775 (lactone), 1715 (ester); δ_{H} 7.25 (m, 4 H, ArH), 7.00 (dd, J 8.37, 4.32, 1 H, 5-H), 6.89 (d, J 5.82, 1 H, 4-H), 6.72 (dd, J 7.11, 7.50, 1 H, 7-H), 6.53 (d, J 6.61, 1 H, 8-H), 6.44 (d, J 6.86, 1 H, 10-H), 4.32 (q, J 7.02, 2 H, OCH_2CH_3), 4.14 (m, 1 H, bridgehead), 2.30 (s, 3 H, CH_3), 1.36 (t, J 7.10, 3 H, OCH_2CH_3); δ_{C} 168.34, 162.65, 161.84, 161.30, 146.18, 144.74, 138.02, 133.98, 133.36, 130.74, 128.91, 128.66, 119.09, 112.40, 87.38, 61.41, 41.39, 21.73, 14.17; m/z (HRMS) 334.121144 (M^+ , $\text{C}_{21}\text{H}_{18}\text{O}_4$ requires M , 334.120509).

Preparation of, and data for, 3e

Reaction of **1b** (0.1 g, 0.53 mmol) and phenylacetylene **2a** (0.108 g, 1.06 mmol), as described earlier for **3a**, yielded **3e** (0.071 g, 79%) as a yellow solid (mp 125–127 °C). The unchanged furanone (0.042 g) was recovered. Product **3e** showed (Found: C, 78.65; H, 4.81. $\text{C}_{19}\text{H}_{14}\text{O}_3$ requires C, 78.61; H, 4.86%); ν_{\max} (KBr)/ cm^{-1} 1775 (lactone), 1688 (C=O); δ_{H} 7.28 (m, 5 H, Ar), 7.16 (dd, J 3.52, 2.30, 1 H, 5-H), 7.01 (d, J 5.95, 1 H, 4-H), 6.74 (dd, J 7.52, 6.57, 1 H, 7-H), 6.58 (d, J 6.52, 1 H, 8-H), 6.47 (d, J 7.25, 1 H, 10-H), 4.16 (m, 1 H, bridgehead), 2.54 (s, 3 H, CH_3); δ_{C} 195.06, 162.22, 147.23, 144.82, 138.76, 134.06, 133.44, 129.38, 128.70, 128.53, 128.18, 124.54, 119.53, 117.69, 87.32, 41.73, 30.40.

Preparation of, and data for, 3f

Reaction of **1b** (0.188, 1 mmol) and *p*-chlorophenylacetylene **2b** (0.273 g, 2 mmol), as described earlier for **3a**, yielded **3f** (0.12 g, 63.7%) as a yellow solid (mp 163–165 °C). The unchanged furanone (0.079 g) was recovered. Product **3f** had (Found: C, 70.35; H, 4.01. $\text{C}_{19}\text{H}_{13}\text{ClO}_3$ requires C, 70.27; H, 4.03%); ν_{\max} (KBr)/ cm^{-1} 1775 (lactone), 1681 (C=O); δ_{H} 7.22–7.03 (m, 4 H, ArH), 6.93 (m, 2 H, 4- and 5-H), 6.67 (dd, J 7.41, 6.86, 1 H, 7-H), 6.51 (d, J 6.64, 1 H, 8-H), 6.41 (d, J 7.78, 1 H, 10-H), 4.08 (m, 1 H, bridgehead), 2.47 (s, 3 H, CH_3); δ_{C} 194.58, 161.63, 146.58, 143.93, 134.42, 133.82, 133.30, 132.63, 131.72, 130.02, 128.71, 128.39, 119.67, 117.73, 86.84, 41.64, 30.30.

Preparation of, and data for, 3g

Reaction of **1b** (0.188, 1 mmol) and *p*-methoxyphenylacetylene **2c** (0.198 g, 1.5 mmol), as described earlier for **3a**, yielded **3g** (0.040 g, 49%) as a yellow solid (mp 190–192 °C). The unchanged furanone (0.14 g) was recovered. Product **3g** had (Found: C, 74.91; H, 4.93. $\text{C}_{20}\text{H}_{16}\text{O}_4$ requires C, 74.99; H, 5.03%); ν_{\max} (KBr)/ cm^{-1} 1757 (lactone), 1682 (C=O); δ_{H} 7.12–6.98 (m, 4 H, ArH), 6.83 (m, 2 H, 4- and 5-H), 6.72 (dd, J 7.40, 6.82, 1 H, 7-H), 6.51 (d, J 6.63, 1 H, 8-H), 6.46 (d, J 7.79, 1 H, 10-H), 4.12 (m, 1 H, bridgehead), 3.78 (s, 3 H, OCH_3), 2.53 (s, 3 H, CH_3); δ_{C} 194.70, 170.26, 162.06, 159.59, 147.03, 144.49, 133.78, 133.33, 130.19, 130.00, 126.47, 119.54, 117.59, 113.59, 87.23, 55.03, 41.67, 30.28.

Photolysis product 4a

A degassed solution of **3a** (0.05 g, 0.16 mmol) in acetonitrile (200 mL) was irradiated in a Pyrex glass tube using the 300 nm lamp in a Rayonet Photochemical Reactor for 1 h. The solvent was removed *in vacuo* and the crude product was chromatographed on a silica gel using 2% ethyl acetate–hexane as eluent to afford the product **4a** (0.035 g, 70%) as light yellow crystals, which were recrystallized from hexane–dichloromethane (mp 139–141 °C); ν_{\max} (KBr)/ cm^{-1} 1775 (lactone), 1715 (ester); δ_{H} 7.32 (d, J 9.82, 1 H, 4-H), 7.27–7.14 (m, 5 H, Ph), 6.43 (dd, J 9.78, 4.65, 1 H, 5-H), 6.18 (dd, J 5.37, 2.41, 1 H, 8-H), 5.47 (d, J 5.34, 1 H, 9-H), 4.36 (q, J 7.11, 2 H, OCH_2CH_3), 3.25 (m, 1 H, 6-H), 2.59 (m, 1 H, 7-H), 1.40 (t, J 7.11, 3 H, OCH_2CH_3); δ_{C} 171.93, 163.66, 160.59, 157.98, 148.54, 137.23, 132.99, 129.32, 128.45, 128.24, 124.03, 120.25, 90.68, 61.05, 53.80, 48.90, 35.57, 14.18; m/z (EI) 322 ($\text{M}^+ + 2$, 1%), 321 ($\text{M}^+ + 1$, 2), 320 (M^+ , 100), 272 (2), 274 (100), 246 (2), 189 (3); m/z (HRMS) 320.103651 (M^+ , $\text{C}_{20}\text{H}_{16}\text{O}_4$ requires M , 320.104859).

Crystal data of **4a**: \dagger $\text{C}_{20}\text{H}_{16}\text{O}_4$. M , 320.33. Crystal size 0.40 × 0.38 × 0.26 mm³. Monoclinic. Space group $P2_1/n$. Unit-cell dimensions $a = 7.4089(1)$, $b = 10.5805(2)$, $c = 20.2337(3)$ Å; $\alpha = 90^\circ$, $\beta = 90.491(1)^\circ$, $\gamma = 90^\circ$. Final R indices [$I > 2\sigma(I)$] $R1 = 0.0377$, $wR2 = 0.0892$. R -indices (all data) $R1 = 0.0603$, $wR2 = 0.1003$. Volume = 1586.06(4) Å³. $D_{\text{calc}} = 1.341$ Mg m⁻³. $F(000) = 672$. Absorption coefficient = 0.093 mm⁻¹. Reflections collected = 27 860 (G. M. Sheldrick, Siemens, Analytical X-ray Division, Madison, WI, 2000).

Photolysis product 4b

Irradiation of **3b** (0.051 g, 0.143 mmol), as described earlier for **4a**, yielded **4b** (0.04 g, 78%) as light yellow crystals, which were recrystallized from hexane–dichloromethane (mp 195–197 °C). Product **4b** showed (Found: C, 67.82; H, 4.20. $\text{C}_{20}\text{H}_{15}\text{ClO}_4$ requires C, 67.70; H, 4.23%); ν_{\max} (KBr)/ cm^{-1} 1775 (lactone), 1715 (ester); δ_{H} 7.33 (d, J 9.84, 1 H, 4-H), 7.27–7.10 (m, 4 H, ArH), 6.43 (dd, J 9.76, 4.71, 1 H, 5-H), 6.18 (dd, J 5.27, 2.31, 1 H, 8-H), 5.48 (d, J 5.29, 1 H, 9-H), 4.37 (q, J 7.14, 2 H,

\dagger CCDC reference number 207/475. See <http://www.rsc.org/suppdata/pl/b0/b005377p> for crystallographic files in .cif format.

OCH₂CH₃), 3.21 (m, 1 H, 6-H), 2.58 (m, 1 H, 7-H), 1.40 (t, *J* 7.12, 3 H, OCH₂CH₃); δ_{C} 172.01, 168.29, 160.47, 151.02, 140.02, 136.83, 133.13, 132.86, 132.59, 130.69, 128.70, 124.11, 90.44, 61.12, 52.86, 48.88, 35.37, 14.16; *m/z* (EI) 355 (M⁺, 2%), 331 (2), 319 (4), 84 (4), 49 (100).

Photolysis product 4c

Irradiation of **3e** (0.050 g, 0.17 mmol) for 10 min as described earlier for **4a** afforded **4c** (0.04 g, 80%) as light yellow crystals, which were recrystallized from hexane–dichloromethane (mp 150–152 °C); ν_{max} (KBr)/cm⁻¹ 1755 (lactone), 1681 (C=O); δ_{H} 7.47 (d, *J* 9.78, 1 H, 4-H), 7.27–7.14 (m, 5 H, Ph), 6.46 (dd, *J* 9.73, 4.61, 1 H, 5-H), 6.18 (dd, *J* 5.14, 2.07, 1 H, 8-H), 5.46 (d, *J* 5.34, 1 H, 9-H), 3.25 (m, 1 H, 6-H), 2.59 (m, 1 H, 7-H), 2.51 (s, 3 H, CH₃); δ_{C} 193.34, 171.90, 169.13, 138.30, 132.48, 129.31, 128.41, 128.27, 124.62, 117.77, 90.78, 54.54, 49.53, 35.59, 29.55; *m/z* (EI) 292 (M⁺ + 2, 2%), 291 (M⁺ + 1, 10), 290 (M⁺, 47), 262 (29), 248 (79), 191 (86), 189 (73), 165 (53), 152 (21), 84 (34), 49 (47), 43 (100); *m/z* (HRMS) 290.09520 (M⁺. C₁₉H₁₄O₃ requires *M*, 290.09430).

Photolysis product 4d

Irradiation of **3f** (0.050 g, 0.15 mmol) for 10 min as described earlier for **4a** afforded **4d** (0.047 g, 94%) as light yellow crystals, which were recrystallized from hexane–dichloromethane (mp 195–197 °C); ν_{max} (KBr)/cm⁻¹ 1758 (lactone), 1681 (C=O); δ_{H} 7.48 (d, *J* 9.82, 1 H, 4-H), 7.30–7.10 (m, 4 H, ArH), 6.46 (dd, *J* 9.80, 4.66, 1 H, 5-H), 6.19 (dd, *J* 5.36, 2.32, 1 H, 8-H), 5.34 (d, *J* 5.34, 1 H, 9-H), 3.23 (m, 1 H, 6-H), 2.58 (m, 1 H, 7-H), 2.52 (s, 3 H, CH₃); δ_{C} 193.23, 171.48, 137.88, 134.39, 133.25, 133.02, 132.56, 130.71, 129.23, 128.72, 128.47, 124.74, 90.56, 53.58, 49.53, 35.36, 29.54; *m/z* (HRMS) 324.054134 (M⁺. C₁₉H₁₃ClO₃ requires *M*, 324.055322).

Acknowledgements

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