Dye-Sensitized Photooxidation of 6-Acyl- and 6-Carboalkoxybenzocycloalken-5-ones: Reaction of Singlet Oxygen with Enolic 1,3-Dicarbonyl Compounds

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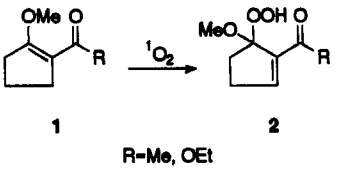
Dye-sensitized photooxidation of alkenes has received much attention from both synthetic and mechanistic points of view.[2] Since singlet oxygen is weakly electrophilic,[3] reactions with electron-rich alkenes such as enol ethers,[4] enamines,[5] and highly substituted olefins[2b] take place readily. By contrast, reactions with electron-poor alkenes such as α,β-unsaturated ketones and esters are often slow or unsuccessful.[6] Regioselective reactions of these compounds with singlet oxygen, where oxygen abstracts hydrogen from the alkyl group geminal to the carbonyl group, have been reported.[7] Enolic tautomers of 1,3-dicarbonyl compounds have received very little attention in singlet oxygen reactions.[8] Ensley et al. reported regioselective photooxygenation of β-alkoxy cyclic enones **1** to give unsaturated hemiperketals **2**.[9] We have recently reported that the enolic tautomer of 2-isobutyryl-4,4-dimethyl-3,4-dihydronaphthalen-1(2*H*)-one (**3**) reacted with singlet oxygen to give the dehydrogenated product **4**.[10] In relation to our studies on the photooxidation of enolic 1,3-diketones,[10,11] we report here the photooxidation of enolic tautomers of 6-acyl and 6-carboalkoxybenzocycloalken-5-ones with singlet oxygen. This reaction gives 6-hydroperoxybenzocycloalkenones which are unexpected products from geminal selectivity and readily deoxygenated by triphenylphosphine to give 6-hydroxybenzocycloalkenones.

Results and Discussion

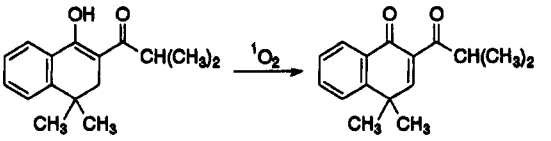
The 6-acyl- and 6-carboalkoxybenzocycloalkenones **5** and **9** were prepared according to previously reported methods.[10,12] The 6-acyl compounds **5a–d** and **9a–c,f** and 6-carbomethoxybenzocyclooctenone (**9g**) exist in the enol form in solution,[10] but 6-carboalkoxy compounds **5e,f** and **9d,e** exist as a enol–keto mixture.

Scheme I



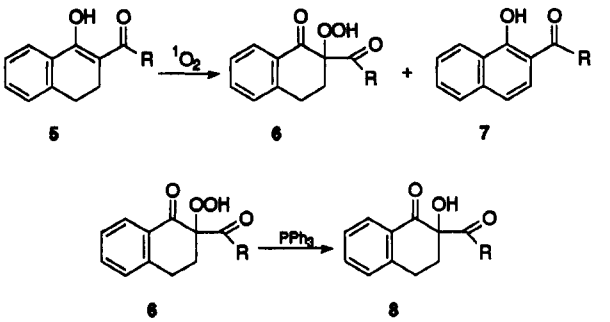
1 **2**

R=Me, OEt



3 **4**

Scheme II



5 **6** **7**

6 **8**

a: R=Me; b: R=Et; c: R=*i*-Pr; d: R=Ph; e: R=OMe; f: R=OEt

Irradiation of 2-acetyl-3,4-dihydronaphthalen-1(2*H*)-one (**5a**) in methanol in the presence of rose bengal as a sensitizer under bubbling air at room temperature with a tungsten–halogen lamp (K_2CrO_4 solution filter) gave 2-acetyl-2-hydroperoxy-3,4-dihydronaphthalen-1(2*H*)-one (**6a**) and 2-acetyl-1-naphthol (**7a**)[13] in 58 and 36% yield, respectively, at 89% conversion.[14] The structure of **6a** was determined on the basis of elemental analysis and spectral data. The ^1H NMR spectrum showed a singlet at δ 11.45 due to OOH. The ^{13}C NMR spectrum showed two carbonyl carbons at δ 199.4 and 206.5 and a quaternary carbon due to C-2 at δ 91.7. Deoxygenation of **6a** in benzene using triphenylphosphine gave the corresponding hydroxynaphthalene (**8a**) which showed a hydroxy ^1H NMR peak at δ 4.60. Photooxidation of naphthalenones **5b–f** under the same conditions also gave the corresponding hydroperoxynaphthalenones **6b–f** and naphthols **7b–f**.[13] Photooxidation of **5a–f** in acetonitrile using methylene blue or rose bengal as a sensitizer gave results similar to those in methanol, whereas that of **5a** in dichloromethane resulted in rapid bleaching of the sensitizer and recovery of a large amount of **5a**. Deoxygenation of **6b–f** gave the corresponding hydroxynaphthalenones **8b–f**. The results of the dye-sensitized photooxidation of **5** are summarized in Table I.

(1) (a) Saitama University. (b) Tokyo Gakugei University.
(2) For general reviews of the reactions of singlet oxygen, see: (a) Frimer, A. A. *Chem. Rev.* **1979**, *79*, 359. (b) *Singlet Oxygen*; Wasserman, H. H., Murray, R. W., Eds.; Academic Press: New York, 1979. (c) Stephenson, L. M.; Grdina, M. S.; Orfanopoulos, M. *Acc. Chem. Res.* **1980**, *13*, 419. (d) *Singlet Oxygen*; Frimer, A. A., Ed.; CRC Press: Boca Raton, FL, 1985.
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0022-3263/93/1958-0278$04.00/0

Table I. Dye-Sensitized Photooxidation of 5 in Acetonitrile[a]

compd	dye	conv[b] (%)	yield[c] (%) 6	yield[c] (%) 7	8[d] (%)
5a	MB[e]	100	43	20	89
5a	RB[f]	97	61	16	
5b	MB	55	31	17	67
5b	RB	97	67	10	
5c	MB	89	33	19	100
5c	RB	52	20	10	
5d	MB	92	66	6	66
5d	RB	80	97	trace	
5e	MB	75	39	7	75
5e	RB	59	36	9	
5f	MB	68	47	16	71
5f	RB	63	64	14	

[a] The reaction of 5 with singlet oxygen in methanol has already been reported; see ref 14. [b] Based on the amount of unchanged starting material recovered after chromatography. [c] Based on converted starting material. [d] Yield of 8 obtained by deoxygenation of 6 with triphenylphosphine. [e] Methylene blue. [f] Rose bengal.

Thus, the reaction of 5 with singlet oxygen provides a new method for the preparation of the 2-hydroxynaphthalenone 8 via the 2-hydroperoxynaphthalenone 6 which is not produced by direct irradiation in the presence of oxygen. Irradiation of 5 with Pyrex-filtered light under bubbling air gave only the naphthol 7.[10] The reaction of singlet oxygen with seven- and eight-membered benzocycloalkenones 9 is also expected to give 6-hydroperoxy compounds.[15] When 6-acetyl- and 6-propionylbenzocyclohepten-5-ones **9a** and **9b** in methanol or acetonitrile were irradiated under bubbling air using methylene blue as a sensitizer, 6-hydroperoxy-6,7,8,9-tetrahydrobenzocyclohepten-5-ones **10a** and **10b** were obtained as very unstable oils. The formation of them was confirmed, just after isolation, by their ^{1}H NMR OOH signals which appeared at δ 10.3 for **10a** and 10.2 for **10b**. Irradiation of 6-isobutyrylbenzocyclohepten-5-one **9c** in methanol or acetonitrile under the same conditions gave 6-hydroperoxybenzocycloheptenone **10c** in 86 or 78% yield, respectively. Photooxidation of 6-carbomethoxy and 6-carbethoxy compounds **9d** and **9e** under the same conditions also gave the corresponding 6-hydroperoxy compounds **10d** and **10e**. The compounds **10a–e** were readily deoxygenated by triphenylphosphine to give the corresponding 6-hydroxy compounds **11a–e**. The compounds **10c** and **11c** were obtained as crystals and compounds **10a,b,d,e** and **11a,b,d,e** were obtained as oils. Microanalysis of **10a,b,d,e** could not be achieved because these compounds decomposed on distillation, but their structures could be elucidated by their spectral data. The ^{1}H NMR spectra of **10** and **11** were very similar except for OOH and OH peaks. The hydroperoxy proton of **10c** appeared at δ 10.38 and the hydroxy proton of **11c** at δ 4.81. The ^{1}H NMR spectra of **10a,b,d,e** showed a peak due to OOH at δ 10.2–10.6. The hydroxy proton of **11a,b,d,e** appeared at δ 4.4–4.8. Benzocyclooctenones **9f** and **9g** also underwent photooxygenation to yield **10f** and **10g** which were deoxygenated to give **11f** and **11g**. The results of the dye-sensitized photooxidation of 9 are summarized in Table II.

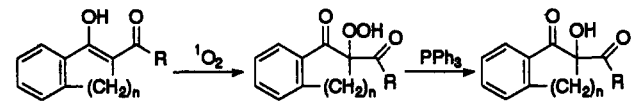
(15) Irradiation of 6-isobutyrylbenzocycloheptenone **9c** and -octenone **9f** which existed completely in the enol form in solution with Pyrex-filtered light under bubbling air gave oxygenated products by the reaction of molecular oxygen with the type-II biradical generated via initial ketonization and subsequent type-II reaction; see: (a) Reference 10. (b) Markov, P. *Chem. Soc. Rev.* **1984**, *13*, 69. (c) Yoshioka, M.; Suzuki, T.; Oka, M. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 1604. (d) Yoshioka, M.; Saitoh, M.; Arai, H.; Ichikawa, K.; Hasegawa, T. *Tetrahedron* **1987**, *43*, 5237.

Table II. Methylene Blue-Sensitized Photooxidation of 9

compd	solvent	conv[a] (%)	10[b] (%)	11[c] (%)
9a	MeCN	69	83	51
9b	MeOH	75	50	44
9b	MeCN	82	88	
9c	MeOH	84	86	69
9c	MeCN	100	78	
9d	MeOH	58	45	81
9d	MeCN	89	69	
9e	MeOH	89	70	81
9e	MeCN	87	68	
9f	MeOH	60	79	70
9g	MeCN	100	80	56

[a] Based on the amount of unchanged starting material recovered after chromatography. [b] Based on converted starting material. [c] Yield of 11 obtained by deoxygenation of 10 with triphenylphosphine.

Scheme III



9 10 11

a: n=3, R=Me; b: n=3, R=Et; c: n=3, R=*i*-Pr; d: n=3, R=OMe
e: n=3, R=OEt; f: n=4, R=*i*-Pr; g: n=4, R=OMe

The reaction of 5 and 9 probably takes place through a perepoxide intermediate **A**.[16] Hydroperoxy compounds 6 and 10 would arise from the cleavage of the carbon–oxygen bond *a* and naphthols 7 would be formed through the hydroperoxide (**B**)[10] which arises from the cleavage of the bond *b*. The reaction of singlet oxygen with α,β-unsaturated carbonyl compounds generally shows geminal selectivity.[7] Hydrogen abstraction by singlet oxygen occurs on the alkyl group geminal to the carbonyl group. In the reaction of 5 with singlet oxygen, the product expected from the geminal selectivity is the naphthol 7, the yield of which is less than that of the hydroperoxynaphthalenone 6. In the reaction of 9 with singlet oxygen, the product expected from the geminal selectivity could not be detected. The lack of geminal selectivity may be ascribed to hydrogen bonding between the hydroxyl group and the perepoxide group in the intermediate **A**. The hydrogen bonding would promote the cleavage of the bond *a*. Wasserman and Pickett reported that enolic tautomers of 1,3-diketones reacted with singlet oxygen to produce 1,2,3-triketones in the presence of fluoride ion which enhances the nucleophilicity of enols.[8,17] They postulated the 2-hydroperoxy 1,3-diketone as an intermediate in this reaction. The present work is the first example of isolation of 2-hydroperoxy-1,3-dicarbonyl compounds in the reaction of enolic 1,3-dicarbonyl compounds with singlet oxygen and provides a new method for the preparation of 2-hydroxy-1,3-dicarbonyl compounds.

Experimental Section

Melting points and boiling points were uncorrected. ^{1}H NMR spectra were recorded at 60 MHz or 400 MHz using tetramethylsilane as an internal standard, and the assignment of signals was performed on the basis of a full set of decoupling experiments. ^{13}C NMR spectra were recorded at 100 MHz with $CDCl_3$ as solvent. IR spectra were recorded for solutions in CCl_4 unless otherwise stated. A 100-W tungsten–halogen lamp was used as an irradiation source. 6-Acylbenzocycloalkenones **5a–d** and **9a–c,f** and 6-carboalkoxybenzocycloalkenones **5e,f** and **9d,e,g**

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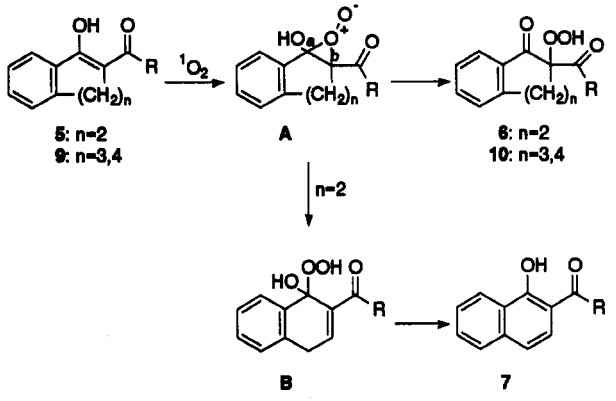
Scheme IV



were prepared according to previously described methods.[10,12] For physical properties of **5c,d** and **9c,f**, see ref 10 for **5c** and **9c,f** and ref 18 for **5d**. The purity of compounds **6b, 10d,g,** and **11a,b,f** was judged to be ≥95%, that of **10e,f** was ≥90%, and that of **10a,b** was ≥70% by ^1H NMR determinations.

General Procedure for Photooxidation. A solution of 500 mg of **5** or **9** in 100 mL of methanol or acetonitrile in the presence of methylene blue or rose bengal (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 (1 g dm^{-3})[19] under bubbling air for 3–15 h. The solvent was removed under reduced pressure, and the residue was chromatographed on silica gel (hexane/ethyl acetate (4:1 to 6:1)) to give **6** and **7** or **10**.

2-Acetyl-2-hydroperoxy-3,4-dihydronaphthalen-1(2*H*)-one (6a): mp 67.5–68.5 °C (hexane); IR ($CHCl_3$) 3350 br, 1710, and 1670 cm^{-1}; ^1H NMR (400 MHz; $CDCl_3$) δ 2.26 (1 H, ddd, *J* = 13.6, 12.2, and 5.0 Hz) and 2.40 (1 H, dt, *J* = 13.6 and 5.0 Hz) (3-H_2), 2.46 (3 H, s, Me), 2.94 (1 H, ddd, *J* = 17.0, 12.2, and 5.0 Hz) and 3.07 (1 H, dt, *J* = 17.0 and 5.0 Hz) (4-H_2), 7.24 (1 H, d, *J* = 7.5 Hz), 7.38 (1 H, t, *J* = 7.5 Hz), 7.54 (1 H, *J* = 7.5 Hz), and 8.05 (1 H, d, *J* = 7.5 Hz) (ArH), and 11.45 (1 H, s, OOH); ^{13}C NMR δ 25.2 (q, Me), 25.7 (t) and 29.2 (t) (C-3 and -4), 91.7 (s, C-2), 127.2 (d), 127.4 (d), 128.7 (d), 131.8 (s), 134.6 (d), and 142.6 (s) (ArC), and 199.4 (s) and 206.5 (s) (2 × C=O). Anal. Calcd for $C_{12}H_{12}O_4$: C, 65.45; H, 5.49. Found: C, 65.29; H, 5.41.

2-Carbethoxy-2-hydroperoxy-3,4-dihydronaphthalen-1(2*H*)-one (6f): mp 72.5 °C (hexane–benzene); IR 3400br, 1730, and 1690 cm^{-1}; ^1H NMR (400 MHz; $CDCl_3$) δ 1.28 (3 H, t, *J* = 7.1 Hz, Me), 2.37 (1 H, ddd, *J* = 13.5, 8.1, and 5.0 Hz) and 2.63 (1 H, ddd, *J* = 13.5, 7.0, and 5.0 Hz) (3-H_2), 2.94 (1 H, ddd, *J* = 17.3, 8.1, and 5.0 Hz) and 3.19 (1 H, ddd, *J* = 17.3, 7.0, and 5.0 Hz) (4-H_2), 4.32 (2 H, t, *J* = 7.1 Hz, OCH_2), 7.26 (1 H, d, *J* = 7.5 Hz), 7.37 (1 H, t, *J* = 7.5 Hz), 7.54 (1 H, t, *J* = 7.5 Hz), and 8.06 (1 H, d, *J* = 7.5 Hz) (ArH), and 10.75 (1 H, s, OOH); ^{13}C NMR δ 14.0 (q, Me), 25.1 (t) and 30.0 (t) (C-3 and C-4), 62.3 (t, OCH_2), 88.1 (s, C-2), 127.1 (d), 128.0 (d), 128.7 (d), 131.0 (s), 134.4 (d), and 142.9 (s) (ArC), 169.3 (s, ester C=O), and 193.7 (s, C=O). Anal. Calcd for $C_{13}H_{14}O_5$: C, 62.39; H, 5.64. Found: C, 62.41; H, 5.62.

6-Hydroperoxy-6-isobutyryl-6,7,8,9-tetrahydrobenzocyclohepten-5-one (10c): mp 98.0–99.0 °C (hexane–benzene); IR ($CHCl_3$) 3400br, 1710, and 1680 cm^{-1}; ^1H NMR (400 MHz; $CDCl_3$) δ 1.12 (3 H, d, *J* = 6.7 Hz) and 1.21 (3 H, d, *J* = 6.7 Hz) (2 × Me), 1.85–2.00 (1 H, m, 8-H), 2.05–2.15 (2 H, m, 7-H and 8-H), 2.44 (1 H, ddd, *J* = 14.7, 8.3, and 4.4 Hz, 7-H), 2.95 (1 H, ddd, *J* = 16.0, 8.4, and 2.8 Hz) and 3.07 (1 H, ddd, *J* = 16.0, 9.0, and 2.8 Hz) (9-H_2), 3.22 (1 H, sept, *J* = 6.7 Hz, COCH), 7.18 (1 H, d, *J* = 7.5 Hz), 7.32 (1 H, t, *J* = 7.5 Hz), 7.42 (1 H, t, *J* = 7.5 Hz), and 7.54 (1 H, d, *J* = 7.5 Hz) (ArH), and 10.38 (1 H, s, OOH); ^{13}C NMR δ 19.8 (q) and 20.0 (q) (2 × Me), 22.8 (t), 31.1 (t), and 34.4 (t) (C-7, -8, and -9), 36.9 (d, COCH), 97.5 (s, C-6), 126.7 (d), 129.4 (2d), 132.0 (d), 138.5 (s), and 139.7 (s) (ArC), and 204.3 (s) and 214.0 (s) (2 × C=O). Anal. Calcd for $C_{15}H_{18}O_4$: C, 68.69; H, 6.92. Found: C, 68.72; H, 7.01.

6-Carbomethoxy-6-hydroperoxy-6,7,8,9-tetrahydrobenzocyclohepten-5-one (10d): an oil; IR 3400br, 1740, and 1700 cm^{-1}; ^1H NMR (400 MHz; $CDCl_3$) δ 1.85–1.95 (1 H, m, 8-H), 2.10–2.20 (2 H, m, 7-H and 8-H), 2.56 (1 H, ddd, *J* = 16.0, 9.0, and 4.6 Hz, 7-H), 2.93 (1 H, ddd, *J* = 14.8, 9.2, and 2.0 Hz, 9-H), 3.10 (1 H, ddd, *J* = 14.8, 8.8, and 2.0 Hz, 9-H), 3.90 (3 H, s, OMe), 7.18 (1 H, d, *J* = 7.5 Hz), 7.31 (1 H, t, *J* = 7.5 Hz), 7.42 (1 H, t, *J* = 7.5 Hz), and 7.59 (1 H, d, *J* = 7.5 Hz) (ArH), and 10.47 (1 H, s, OOH); ^{13}C NMR δ 22.8 (t), 32.2 (t), and 34.7 (t) (C-7, -8, and -9), 53.0 (q, OMe), 94.2 (s, C-6), 126.5 (d), 129.3 (d), 130.0 (d), 131.9 (d), 137.7 (s), and 140.0 (s) (ArC), 171.3 (s, ester C=O), and 200.3 (s, C=O).

6-Carbomethoxy-6-hydroperoxy-7,8,9,10-tetrahydrobenzocycloocten-5(6*H*)-one (10g): an oil; IR 3400br, 1740, and 1700 cm^{-1}; ^1H NMR (400 MHz; $CDCl_3$) δ 1.55–1.85 (4 H, m, 8-H_2 and 9-H_2), 2.10–2.25 (2 H, m, 7-H_2), 2.65 (1 H, ddd, *J* = 15.0, 11.0, and 4.5 Hz) and 2.81 (1 H, dt, *J* = 15.0 and 4.1 Hz) (10-H_2), 3.91 (3 H, s, OMe), 7.16 (1 H, d, *J* = 7.5 Hz), 7.28 (1 H, t, *J* = 7.5 Hz), 7.37 (1 H, t, *J* = 7.5 Hz), and 7.47 (1 H, d, *J* = 7.5 Hz) (ArH), and 10.70 (1 H, s, OOH); ^{13}C NMR δ 18.6 (t), 29.0 (t), 30.1 (t) and 31.1 (t) (C-7, -8, -9, and -10), 52.8 (q, OMe)), 94.3 (s, C-6), 125.6 (d), 126.5 (d), 128.8 (d), 129.7 (d), 136.6 (s), and 139.0 (s) (ArC), 170.9 (s, ester C=O), and 205.2 (s, C=O).

General Procedure for Deoxygenation of 6 and 10. A mixture of the hydroperoxy compound **6** or **10** (100–300 mg) and 1.1 equiv of triphenylphosphine in benzene (10–30 mL) was stirred at room temperature for 3–24 h. Concentration under reduced pressure and subsequent chromatography on silica gel (hexane/ethyl acetate (4:1)) gave the hydroxy compound **8** or **11**.

2-Acetyl-2-hydroxy-3,4-dihydronaphthalen-1(2*H*)-one (8a): mp 58.5–59.5 °C (hexane); IR 3470br, 1720, and 1690 cm^{-1}; ^1H NMR (400 MHz; $CDCl_3$) δ 2.19 (1 H, dt, *J* = 15.3 and 7.9 Hz) and 2.60 (1 H, dt, *J* = 15.3 and 4.9 Hz) (3-H_2), 2.28 (3 H, s, Me), 3.10–3.15 (2 H, m, 4-H_2), 4.60 (1 H, s, OH), and 7.26 (1 H, d, *J* = 7.5 Hz), and 7.35 (1 H, t, *J* = 7.5 Hz), 7.54 (1 H, t, *J* = 7.5 Hz), and 8.02 (1 H, d, *J* = 7.5 Hz) (ArH); ^{13}C NMR δ 25.0 (q, Me), 25.5 (t) and 32.3 (t) (C-3 and -4), 81.8 (s, C-2), 126.9 (d), 127.8 (d), 129.0 (d), 130.4 (s), 134.5 (d), and 144.2 (s) (ArC), and 196.6 (s) and 206.8 (s) (2 × C=O). Anal. Calcd for $C_{12}H_{12}O_3$: C, 70.58; H, 5.92. Found: C, 70.40; H, 5.87.

2-Carbethoxy-2-hydroxy-3,4-dihydronaphthalen-1(2*H*)-one (8f): bp 115 °C (0.7 Torr); IR 3500br, 1740, and 1690 cm^{-1}; ^1H NMR (400 MHz; $CDCl_3$) δ 1.22 (3 H, t, *J* = 7.1 Hz, Me), 2.25 (1 H, dt, *J* = 14.6 and 7.1 Hz) and 2.72 (1 H, dt, *J* = 1.46 and 5.0 Hz) (3-H_2), 3.10–3.20 (2 H, m, 4-H_2), 4.22 (2 H, q, *J* = 7.1 Hz, OCH_2), 4.31 (1 H, s, OH), 7.27 (1 H, d, *J* = 7.5 Hz), and 7.35 (1 H, t, *J* = 7.5 Hz), 7.54 (1 H, t, *J* = 7.5 Hz) and 8.05 (1 H, d, *J* = 7.5 Hz) (ArH); ^{13}C NMR δ 13.6 (q, Me), 25.3 (t) and 32.5 (t) (C-3 and -4), 62.0 (t, OCH_2), 77.4 (s, C-2), 126.7 (d), 127.9 (d), 128.7 (d), 130.1 (s), 134.1 (d), and 143.8 (s) (ArC), 170.6 (s, ester C=O), and 194.4 (s, C=O). Anal. Calcd for $C_{13}H_{14}O_4$: C, 66.66; H, 6.02. Found: C, 66.64; H, 5.99.

6-Hydroxy-6-isobutyryl-6,7,8,9-tetrahydrobenzocyclohepten-5-one (11c): mp 52.5 °C (pentane); IR 3450br, 1720, and 1685 cm^{-1}; ^1H NMR (400 MHz; $CDCl_3$) δ 0.88 (3 H, d, *J* = 6.7 Hz) and 1.10 (3 H, d, *J* = 6.7 Hz) (2 × Me), 1.85 (1 H, dt, *J* = 14.0 and 5.2 Hz, 7-H), 1.90–2.10 (2 H, m, 8-H_2), 2.50 (1 H, ddd, *J* = 14.0, 9.7, and 5.4 Hz, 7-H), 2.87 (1 H, sept, *J* = 6.7 Hz, COCH), 2.98 (1 H, ddd, *J* = 15.5, 11.1, and 6.5 Hz) and 3.08 (1 H, ddd, *J* = 15.5, 8.8, and 4.9 Hz) (9-H_2), 4.81 (1 H, s, OH), and 7.21 (1 H, d, *J* = 7.5 Hz), 7.29 (1 H, t, *J* = 7.5 Hz), and 7.40–7.50 (2 H, m) (ArH); ^{13}C NMR δ 19.4 (q) and 19.9 (q) (2 × Me), 22.3 (t) and 33.6 (2 × t) (C-7, -8, and -9), 36.3 (d, COCH), 87.1 (s, C-6), 126.5 (d), 128.8 (d), 129.7 (d), 132.4 (d), 137.4 (s), and 140.7 (s) (ArC), and 205.2 (s) and 211.8 (s) (2 × C=O). Anal. Calcd for $C_{15}H_{18}O_3$: C, 73.15; H, 7.37. Found: C, 73.09; H, 7.37.

6-Carbomethoxy-6-hydroxy-6,7,8,9-tetrahydrobenzocyclohepten-5-one (11d): bp 112–115 °C (0.4 Torr); IR 3500br, 1760, and 1700 cm^{-1}; ^1H NMR (400 MHz; $CDCl_3$) δ 1.85–2.10 (3 H, m, 7-H and 8-H_2), 2.50–2.60 (1 H, m, 7-H), 2.89 (1 H, ddd, *J* = 15.0, 6.0, and 3.6 Hz) and 3.00 (1 H, ddd, *J* = 15.0, 9.3, and 4.3 Hz) (9-H_2), 3.68 (3 H, s, OMe), 4.41 (1 H, s, OH), and 7.18 (1 H, d, *J* = 7.5 Hz), 7.29 (1 H, t, *J* = 7.5 Hz), 7.42 (1 H, t, *J* = 7.5 Hz), and 7.50 (1 H, d, *J* = 7.5 Hz) (ArH); ^{13}C NMR δ 22.3 (t) and 33.7

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(2 × t) (C-7, -8, and -9), 52.7 (q, OMe), 81.8 (s, C-6), 126.4 (d), 129.1 (d), 129.3 (d), 132.1 (d), 137.0 (s), and 139.7 (s) (ArC), 171.2 (s, ester C=O), and 204.1 (s, C=O). Anal. Calcd for $C_{13}H_{14}O_4$: C, 66.66; H, 6.02. Found: C, 66.72; H, 5.99.

6-Carbomethoxy-6-hydroxy-7,8,9,10-tetrahydrobenzocycloocten-5(6*H*)-one (11g): bp 110 °C (0.7 Torr); IR 3480br, 1750, and 1710 cm^{-1}; ^1H NMR (400 MHz; $CDCl_3$) δ 1.55–1.70 (2 H, m) and 1.75–1.90 (2 H, m) (8-H_2 and 9-H_2), 2.10 (1 H, ddd, J = 15.1, 6.8 and 2.3 Hz) and 2.28 (1 H, dd, with t-character, J = 15.1 and 12.2 Hz) (7-H_2), 2.80 (2 H, t, J = 6.0 Hz, 10-H_2), 3.73 (3 H, s, OMe), 4.69 (1 H, s, OH), and 6.92 (1 H, d, J = 7.5 Hz), 7.15–7.25 (2 H, m), and 7.34 (1 H, t, J = 7.5 Hz) (ArH); ^{13}C NMR δ 22.1 (t), 26.6 (t), 31.4 (t), and 33.1 (t) (C-7, -8, -9, and C-10), 52.8 (q, OMe), 84.5 (s, C-6), 125.5 (d), 126.0 (d), 129.8 (d), 129.9 (d), 136.6 (s), and 139.0 (s) (ArC), 169.9 (s, ester C=O), and 207.7 (s, C=O). Anal. Calcd for $C_{14}H_{16}O_4$: C, 67.73; H, 6.50. Found: C, 67.65; H, 6.46.

Supplementary Material Available: Spectral data (IR, ^1H NMR, ^{13}C NMR), melting points or boiling points, and elemental analysis data of **5a,b,e,f**, **9a,b,d,e,g**, **6c–e**, **8b–e**, and **11e**, ^1H and ^{13}C NMR spectra of **6b**, **10d,f,g** and **11a,f**, and ^1H NMR spectra of **10a,b,e** and **11b** (20 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.