# Photoinduced Molecular Transformations. Part 138.[1] A New Route to Dibenzo[a,d]cycloalkanes and their Naphtho Analogues via the Ring Expansion of Benzocyclobutenols involving a Selective β-Scission of Cyclobutenoxyl Radicals Generated by Photolysis of their Hypoiodites

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A new synthesis of several funtionalized dibenzo[a,d]cyclooctanes, dibenzo[a,d]cyclononanes, and their naphtho analogues is described. This synthesis involves the ring expansion of benzocyclo-butenols by a selective β-scission of the cyclobutenoxyl radicals generated by photolysis of their hypoiodites.

Our previous studies concerning applications of hypoiodite photochemistry to organic transformations have indicated that the fragmentation of alkoxyl radicals generated from appropriate hypoiodites by irradiation takes place in a highly selective manner, and is useful in organic synthesis.

We have, thus, demonstrated the utility of selective radical fragmentation in organic synthesis by synthesizing a variety of organic compounds, including natural products.[1,2] A process involving the selective β-scission of a fused β bond to the alkoxyl radicals generated from the hypoiodites of several catacondensed lactols or catacondensed bicyclic tertiary alcohols (outlined in general Scheme 1) was shown to be one of the most powerful methods for ring expansions leading to medium-sized lactones,[2e,g] macrolides,[2h] and the macrocyclic ketones,[2f] such as (±)-muscone.


Scheme 1
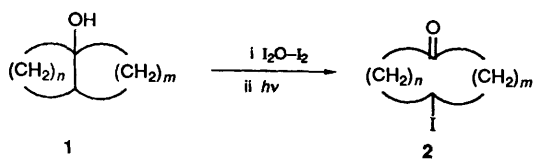
In this paper we report on a new general synthesis of dibenzo[a,d]cycloalkanes and their naphtho analogues, based on this approach. This new synthesis involves the ring expansion of benzocyclobutenols by a selective β-scission of the cyclobutenoxyl radicals generated by photolysis of the hypoiodites of benzocyclobutenols 3, as outlined in Scheme 2.
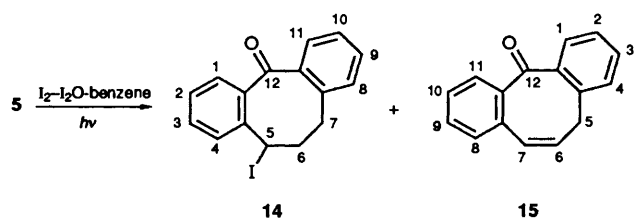

Scheme 2
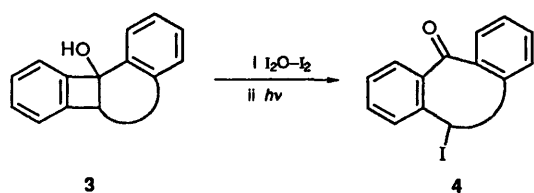
Results

The two benzocyclobutenols, cis-5,6,6a,10b-tetrahydrobenzo-[a]biphenylen-10b-ol 5[3,4] and 11b-hydroxy-cis-5,6,7,7a,tetra-hydro-11bH-benzo[a]benzo[3,4]cyclobuta[1,2-c]cyclohepten-11b-ol 6[4,5] for ring expansion were prepared according to a published method.[4] In addition to these, naphthocyclobutenols 9, 10, 12 and 13 were newly prepared according to the same method, as outlined in Scheme 3. Thus, the reaction of 1-

Scheme 3
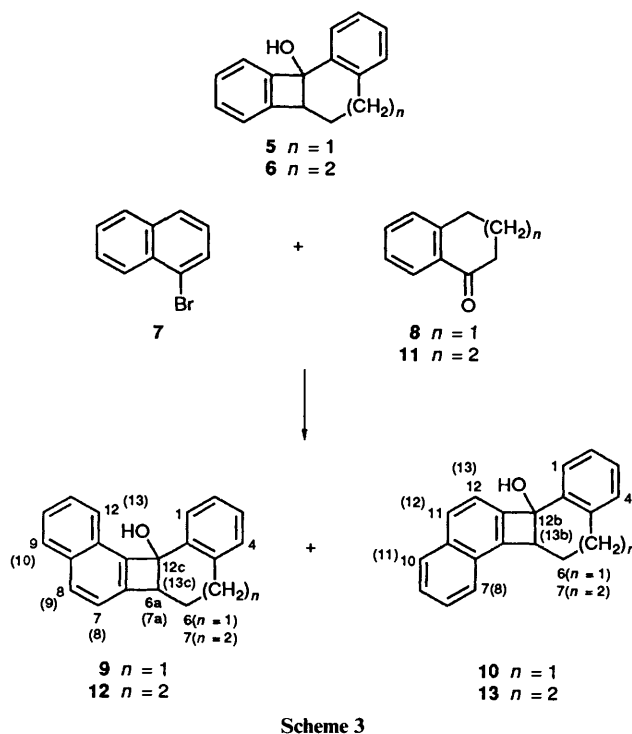
bromonaphthalene 7 with 1-tetralone 8 in the presence of sodium amide in THF under the reported procedure gave cis-tetrahydrodibenzobiphenylen-12c-ol 9 and cis-tetrahydrodi-benzobiphenylen-12b-ol 10 in 28 and 4.8% yields, respectively. The reaction of 1-bromonaphthalene 7 with benzosuberone 11 gave cis-tetrahydrobenzonaphthocyclobutacyclohepten-13b-ol 12 and cis-tetrahydrobenzonaphthocyclobutacyclohepten-13c-ol 13 in 43 and 8.4% yield, respectively. Their structures were established by analysing the structure of the products derived from the β-scission reaction (see below).

Synthesis of Functionalized Dibenzo[a,d]cycloalkanes 14, 15, 16 and 17 and Their Naphtho Analogues 18, 19 and 20.—Irradiation of the hypoiodite of the benzocyclobutenol 5, prepared in situ by a treatment with red mercury(II) oxide and iodine (each 3 mol equiv.) in benzene according to our standard method,[2] gave a major product 14 (59%) and a minor one 15 (19%). These products could be readily isolated by preparative TLC (PLC). High-resolution mass spectrometry and combustion analysis have indicated that their molecular formulae were $C_{16}H_{13}IO$ and $C_{16}H_{12}O$, respectively. The IR spectra of both
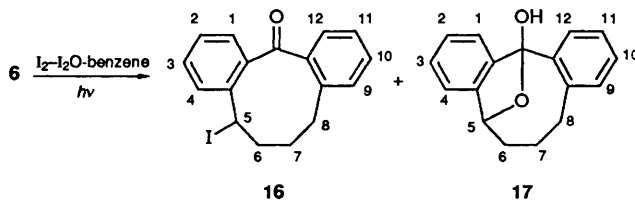
Scheme 4

Scheme 6

products **14** and **15** (see Experimental section) have indicated that they are ketones arising from the expected ring expansion.

The ¹H NMR spectrum of the ketone **14** exhibited a double doublet signal at δ 5.33, which is assignable to a proton attached to the carbon carrying an iodine atom. These and other spectral results, together with the expected reaction pathway, have indicated that product **14** was 5-iodo-6,7-dihydrodibenzo[a,d]cycloocten-12(5H)-one, arising from a β-scission of the fused bond of the alkoxyl radical generated from the benzocyclobutenol **5**.

The ¹H NMR spectrum of the minor ketone **15** exhibited two signals (each 1 H) at δ 6.08 and 6.80 which are assignable to the olefinic protons. This result together with the expected reaction pathway have enabled us to assign dibenzo[a,d]cyclo-octen-12(5H)-one as the structure of the ketone **15**.

Irradiation of the hypoiodite of the benzocyclobutenol **6** under conditions similar to those of the homologous benzo-cyclobutenol **5** gave a major product **16** (39%) and a minor product **17** (26%). Mass spectrometry and combustion analysis
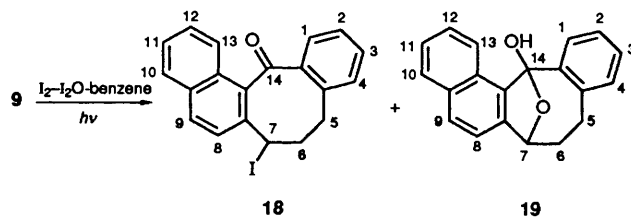

Scheme 5

of these products have established that they have the molecular formulae $C_{17}H_{15}IO$ and $C_{17}H_{16}O_2$, respectively. The IR spectrum of the product **16** exhibited an intense band which is assignable to the carbonyl group, while the IR spectrum of product **17** showed a band due to the hydroxy group. The ¹H NMR spectrum of the ketone **16** exhibited a double doublet signal at δ 5.47 which is assignable to a proton attached to the benzylic carbon carrying an iodine atom (see Experimental section), while the mass spectrum exhibited the parent peak at m/z 235, assignable to the $(M - I)^+$ ion. These results indicated that the product **16** was 5,6,7,8-tetrahydro-5-iodo-13H-dibenzo[a,d]cyclononan-13-one arising from a β-scission of the alkoxyl radical. The ¹H NMR spectrum of the alcohol **17** exhibited a doublet at δ 5.88, assignable to a proton attached to the carbon carrying an oxygen atom. This indicated that product **17** was 5,13-epoxy-6,7,8,13-tetrahydro-5H-dibenzo[a,d]cyclononan-13-ol, arising from a reaction of the 8-membered cyclic carbocation with diiodine oxide [2m] (see below).

An analogous reaction of the hypoiodite generated from naphthocyclobutenol **9** was found to lead to parallel results; irradiation of the hypoiodite of the naphthocyclobutenol **9** under analogous conditions gave a major product **18** (44%) and a more polar minor product **19** (25%).

High-resolution mass spectrometry and combustion analysis established that the molecular formulae of products **18** and **19** were $C_{20}H_{15}IO$ and $C_{20}H_{16}O_2$, respectively. Analysis of the mass, IR, and ¹H NMR spectra of both products indicated that products **18** and **19** were 6,7-dihydro-7-iodo-5H,14H-benzo-

[a]benzo[5,6]benzo[1,2-d]cycloocten-14-one **18** and 7,14-epoxy-5,6,7,14-tetrahydrobenzo[a]benzo[5,6]benzo[1,2-d]cy-cloocten-14-ol **19**, respectively. Details concerning the spectral analysis are described in the Experimental section.

Our final pursuit in this ring-expansion work was made concerning the naphthocyclobutenol **12**. Thus, irradiation of the hypoiodite of the naphthocyclobutenol **12**, prepared *in situ* with mercury(II) oxide and iodine (as described above), afforded a major product **20** (51%) and a less-polar minor product **21** (16%). The high-resolution mass spectrometry and combustion
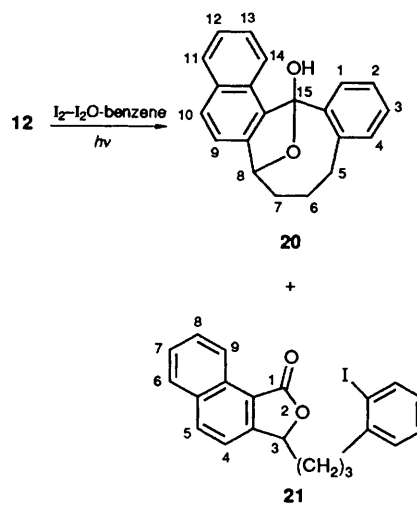
Scheme 7

analysis established the molecular formulae, $C_{21}H_{18}O_2$ and $C_{21}H_{17}IO_2$, for products **20** and **21**, respectively. The IR and ¹H NMR spectra of the major product **20** indicated that it was an acetal homologous to product **19**. The IR spectrum of the minor product **21**, however, exhibited an intense band at 1748 cm⁻¹, assignable to the phthalide carbonyl group. The ¹H NMR spectrum of product **21** exhibited a double doublet signal at δ 5.57, assignable to a proton attached to C-3 of the phthalide skeleton.[2m] The spectrum also exhibited a doublet signal at δ 9.01 with J 8.3, which is assignable to the aromatic proton located at the *peri* position (9-H).[6] The ¹³C NMR spectrum exhibited signals at δ 25.4, 33.8 and 40.3, assignable to -[CH₂]₃-, at δ 80.3, assignable to C-3 of the phthalide skeleton,[7] at δ 100.6 assignable to a phenyl carbon bearing an iodine,[8] and δ 151.4 attributable to the phthalide carbonyl.[7] These results and the expected reaction pathway (*vide infra*) indicated that product **21** was 3-[3-(2-iodophenyl)propyl]-naphtho[1,2-c]furan-1(3H)-one, arising from a secondary fragmentation of the alkoxyl radical generated from product **20**. This result eventually established that the structure of cyclobutenol **12** was cis-5,6,6a,12c-tetrahydrodibenzo[a,i]bi-phenylen-12c-ol and not its isomer **13**, since the signal due to a proton attached to a *peri* position of the phthalide derived from isomer **13** should appear at around δ < 8.4, as reported for their parent compounds.[6]

Scheme 8
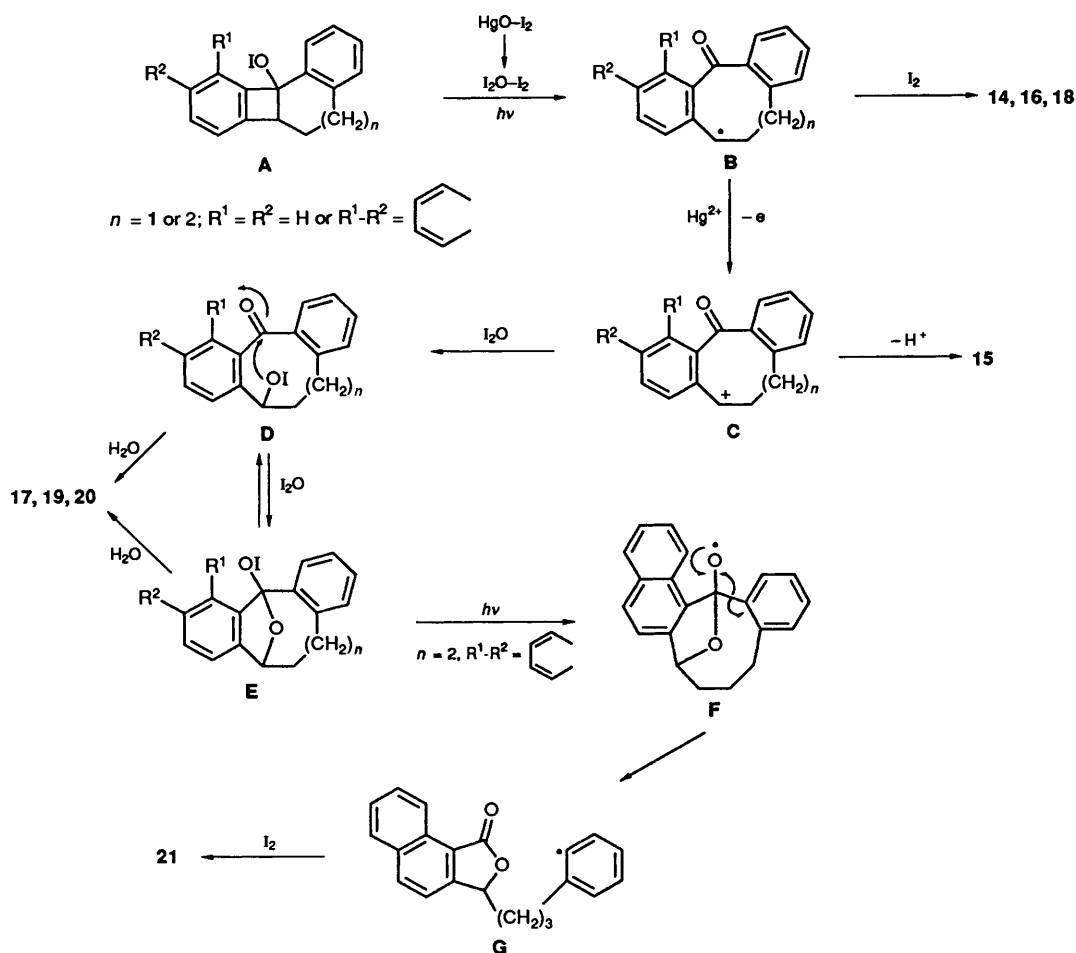
Discussion

The above-mentioned experiments have shown that the alkoxyl radicals generated from the hypoiodites of the fused benzocyclobutenols 5, 6, 9 and 12 by photolysis result in the selective cleavage of the fused bond and give functionalized dibenzo[a,d]cycloalkenes 14–17 (65–78%) and their naphtho analogues 18, 19 and 20 (51–69%).

Several syntheses of dibenzo[a,d]cyclooctenes and dibenzo-[a,d]cyclononenes under rather drastic conditions have been reported. These methods include a base-catalysed ring expansion of tetracyclic benzocyclobutenols,[9] the reaction of 2,2'-bis(bromomethyl)diphenylmethane with sodiomalononitrile,[10] a thermal ring expansion of 8,8-dichloro-2,3:5,6-dibenzobicyclo[5.1.0]octane derivatives,[11] a ring expansion of 2,3:6,7-dibenzocycloheptatriene[12] and others.[13]

The present synthesis of functionalized dibenzo[a,d]cycloalkenes, which takes place under nearly neutral conditions and room temperature, can either complement or replace some of these older methods.

Three types of ring-expansion products can be formed using the present method: iododibenzo[a,d]cycloalkenones 14, 16 and 18; dibenzo[a,d]cycloalkene 15; and transannular hemiacetals 17, 19 and 20. The pathways leading to all of these products are outlined in Scheme 8; irradiation of the hypoiodites A of fused benzocyclobutenols generates a stabilized cyclic benzyl radical B via alkoxyl radicals. These radicals abstract an iodine atom from an excess of iodine in the solution to give iododibenzo[a,d]cycloalkenones 14, 16 and 18. One-electron oxidation of part of the benzyl radical B by a metal ion

generates the coresponding benzyl cation C. Removal of a proton from carbocation C gives a dibenzo[a,d]cycloalkene 15. The carbocations C, on the other hand, react with diiodine oxide to generate a second hypoiodite D and/or E.[2a,m] The transannular hemiacetals 17, 19 and 20 can be formed during a work-up of the solution. There have been ample precedents found by us for the formation of hemiacetals that are similar to these.[2a,g,m] It is interesting to note that no transannular hemiacetal, such as 17, is formed in the photoreaction of the fused benzocyclobutenol 5, while the transannular hemiacetal 20 and phthalide 21 derived from it (vide infra) are exclusive products in the photoreaction of the fused benzocyclobutenol 12. This difference apparently stems partly from the difference in the conformation of the intermediary cyclic benzyl radicals. Thus, among homologous 8-membered and 9-membered hypoiodites D generated from the fused benzocyclobutenols 5 and 6, formation of the transannular hemiacetal is likely to be more facile in the 9-membered hypoiodite, since the ring is more mobile. The same should be true for the case of 8- and 9-membered hypoiodites generated from the naphtho analogues 9 and 12. The foregoing results are in agreement with the assumption.

Finally, the pathway leading to the phthalide derivative 21 should be mentioned. It is clear that 21 is a secondary product formed from the hypoiodite E; photolysis of the hypoiodite E generates the corresponding alkoxyl radical F, which collapses to give the aromatic radical G via a β scission between the aromatic carbon and the benzyl carbon, as outlined in Scheme 8. The phenyl radical G abstracts an iodine atom from an iodine

molecule to give the phthalide **21**. To our knowledge, the scission is the first example of a cleavage of a rather strong aryl–alkyl bond in the β-scission of alkoxyl radicals; this cleavage should be especially favoured by the formation of a conjugated carbonyl.

Experimental

M.p.s were recorded with a Yanagimoto melting-point apparatus and are uncorrected. The IR spectra were determined for Nujol mulls with a JASCO IR-810 spectrometer, unless otherwise stated. The ^{1}H NMR spectra were determined in CDCl$_3$ (SiMe$_4$ as internal reference) with either a Hitachi R-90H FT NMR spectrometer operating at 90 MHz or a JEOL JNM-EX-400 FT NMR spectrometer operating at 400 MHz. *J*-Values are recorded in Hz. High- and low-resolution mass spectra were recorded with a JEOL JMS-DX303 spectrometer. TLC was carried out on Merck Kieselgel 60PF$_{254}$. Photolysis was carried out with a 100-W high-pressure Hg arc lamp (EIKOSHA, EHB-WU-100).

cis-5,6,6a,12c-*Tetrahydrodibenzo*[a,i]*biphenylen*-12c-*ol* **9** *and* cis-5,6,6a,12c-*Tetrahydrodibenzo*[a,g]*biphenylen*-12b-*ol* **10**.— The reaction of 1-bromonaphthalene **7** (1.14 g, 0.55 mmol) with 1-tetralone **8** (730 mg, 5.0 mmol) in the presence of NaNH$_2$ (390 mg, 10 mmol) in THF (10 cm^3) under the conditions reported for the reaction of bromobenzene with 1-tetralone reported by Adam *et al.*[4] gave **9** (386 mg, 28%) and **10** (66 mg, 4.8%). **9**: R_F 0.40 (EtOAc–hexane, 1:3): m.p. 114–115 °C (from Et$_2$O–hexane); ν_{max}/cm^{-1} 3332; δ(400 MHz) 1.92 (1 H, tdd, *J* 13.67, 4.88 and 3.42, 6-H), 2.12 (1 H, ddd, *J* 13.67, 4.40 and 3.91, 5-H), 2.31 (1 H, ddt, *J* 13.67, 3.42 and 2.93, 6-H), 2.64 (1 H, br d, *J* 5.6, 5-H), 3.97 (1 H, br d, *J* 4.9, 6a-H), 7.04 (1 H, d, *J* 7.33), 7.16 (td, *J* 7.33 and 1.47), 7.35–7.45 (4 H, m), 7.75–7.85 (3 H, m) and 8.23 (1 H, dd, *J* 7.82 and 0.98); *m/z* 272 (M$^+$, 6.9), 255 [(M − OH),$^+$ 10] and 244 [(M − CO)$^+$, 100] (Found: C, 88.8; H, 6.0). C$_{20}$C$_{16}$O requires C, 88.20; H, 5.92%). **10**: R_F 0.31 (EtOAc–hexane, 1:3); m.p. 70–74 °C (from Et$_2$O–hexane); ν_{max}/cm^{-1} 3332; δ(400 MHz), 1.95–2.15 (2 H, m, 6-H), 2.53 (1 H, ddd, *J* 13.18, 6.84 and 3.91, 5-H), 2.6–2.75 (2 H, m, OH and 5-H), 4.16 (1 H, dd, *J* 3.91 and 2.93, 6a-H), 7.05 (1 H, d, *J* 7.32), 7.15–7.2 (2 H, m), 7.35 (1 H, dd, *J* 7.81 and 7.32), 7.45–7.55 (2 H, m), 7.71 (1 H, d, *J* 8.30), 7.8–7.9 (2 H, m) and 8.01 (1 H, dd, *J* 7.81 and 0.98); *m/z* 272 (M$^+$, 8.8), 271 [(M − 1)$^+$, 9.0] and 244 [(M − CO)$^+$, 100] (Found: M$^+$, 272.1177. C$_{20}$H$_{16}$O requires *M*, 272.1201).

cis-5,6,7,7a-*Tetrahydro*-13cH-*benzo*[a]*naphtho*[4,3-a]*cyclobuta*[1,2-c]*cyclohepten*-13c-*ol* **12** *and* cis-5,6,7,7a-*Tetrahydro*-13bH-*benzo*[a]*naphtho*[3,4-a]*cyclobuta*[2,1-c]*cyclohepten*-13b-*ol* **13**.—The reaction of 1-bromonaphthalene (2.28 g, 11 mmol) with benzosuberone (tetrahydrobenzocycloheptenone) **11** (1.60 g, 11 mmol) in the presence of NaNH$_2$ (0.78 g, 20 mmol) in THF (10 cm^3) under the conditions of the reaction of bromobenzene with benzosuberone reported by Adams *et al.*[4] gave **12** (1.23 g, 43%) and **13** (0.23 ,g 8.4%): **12** R_F 0.22 (EtOAc–hexane, 1:5); m.p. 55–57 °C (from Et$_2$O–hexane); ν_{max}/cm^{-1} 3320; δ(400 MHz) 1.16 (1 H, qd, *J* 13.18, 6.35), 1.65–1.75 (1 H, m), 1.85–2.0 (1 H, m), 2.08 (1 H, ddd, *J* 13.18, 8.30 and 3.42), 2.6–2.8 and 2.72 (combined 2 H, br s and dd, *J* 13.18 and 6.35, OH and 5-H), 3.5–3.6 (2 H, m, 7a-H and 5-H), 7.1–7.25 (3 H, m), 7.31 (1 H, d, *J* 8.30), 7.45–7.65 (3 H, m), 7.85 (1 H, d, *J* 8.30), 7.92 (1 H, d, *J* 8.30) and 8.15 (1 H, d, *J* 8.30); *m/z* 286 (M$^+$, 88) and 257 (100) (Found: M$^+$, 286.1364. C$_{21}$H$_{18}$O requires *M*, 286.1357); **13** R_F 0.17 (EtOAc–hexane, 1:5); m.p. 138 °C (from Et$_2$O–hexane); ν_{max}/cm^{-1} 3330; δ(90 MHz) 1.2–2.9 (6 H, m), 3.53 (1 H, dt, *J* 13.41 and 6.82, 5-H), 3.78 (1 H, dd, *J* 12.96 and 2.86, 7a-H) and 7.1–7.9 (10 H, m); *m/z* 286 (M$^+$, 83) and 244 (100) (Found: M$^+$, 286.1336. C$_{21}$H$_{18}$O requires *M*, 286.1357).

5-*Iodo*-6,7-*dihydrodibenzo*[a,d]*cycloocten*-12(5H)-*one* **14** *and* Dibenzo[a,d]*cycloocten*-12(5H)-*one* **15**.—A solution of the tetracyclic alcohol **5** (175 mg, 0.79 mmol) in benzene (30 cm^3) containing red mercury(II) oxide (511 mg, 2.36 mmol) and iodine (599 mg, 2.36 mmol) in a Pyrex vessel was irradiated with a 100-W high-pressure mercury arc for 2 h under nitrogen. The resulting mixture was filtered through a Celite pad; the filtrate was washed with aqueous Na$_2$SO$_3$, dried (MgSO$_4$) and evaporated. The resulting residue was subjected to PLC on SiO$_2$. The isolated products were **14** (162 mg, 59%) and **15** (33 mg, 19%): **14** R_F 0.42 (EtOAc–hexane, 1:5); m.p. 133–134 °C (from hexane–CH$_2$Cl$_2$); ν_{max}/cm^{-1} 1637; δ(90 MHz) 2.25–2.7 (4 H, m), 5.33 (1 H, dd, *J* 10.22 and 6.48, 5-H), 7.15–7.85 (7 H, m) and 8.27 (1 H, dd, *J* 7.69 and 1.76); *m/z* 349 [(M + 1)$^+$, 0.21], 348 (M$^+$, 0.07) and 221 [(M − 1)$^+$, 100] (Found: C, 55.1; H, 3.75; I, 36.65. C$_{16}$H$_{13}$IO requires C, 55.20; H, 3.76; I, 36.45); **15** R_F 0.38 (EtOAc–hexane, 1:5); an oil; ν_{max}/cm^{-1} 1655; δ(90 MHz) 3.36 (2 H, d, *J* 8.12, 5-H), 6.08 (1 H, dt, *J* 10.10 and 8.12, 6-H), 6.80 (1 H, d, *J* 10.10, 7-H), 7.05–7.55 (7 H, m) and 8.07 (1 H, dd, *J* 7.03 and 1.98); *m/z* 220 (M$^+$, 100) (Found: M$^+$, 220.0872. C$_{16}$H$_{12}$O requires *M*, 220.0888).

5,6,7,8-*Tetrahydro*-5-*iodo*-13H-*dibenzo*[a,d]*cyclononen*-13-*one* **16** *and* 5,13-*Epoxy*-6,7,8,13-*tetrahydro*-5H-*dibenzo*[a,d]*cyclononen*-13-*ol* **17**.—A similar photolysis of the tetracyclic alcohol **6** (236 mg, 1 mmol) in benzene (40 cm^3) in the presence of red mercury(II) oxide (650 mg, 3 mmol) and iodine (762 mg, 3 mmol) for 50 min gave **16** (141 mg, 39%) and **17** (66 mg, 26%): **16** R_F 0.34 (EtOAc–hexane, 1:5); m.p. 147–148 °C (from hexane–CH$_2$Cl$_2$–Et$_2$O); ν_{max}/cm^{-1} 1661; δ(90 MHz) 1.5–2.0 (2 H, m), 2.3–2.8 (4 H, m), 5.47 (1 H, dd, *J* 11.76 and 6.27, 5-H), 6.95–7.55 (7 H, m) and 8.11 (1 H, dd, *J* 7.59 and 1.98); *m/z* 362 (M$^+$, 0.32) and 235 [(M − I)$^+$, 100] (Found: C, 56.25; H, 4.13. C$_{17}$H$_{15}$IO requires C, 56.37; H, 4.17); **17** R_F 0.10 (EtOAc–hexane, 1:5); m.p. 152–153 °C (from CH$_2$Cl$_2$–hexane); ν_{max}/cm^{-1} 3370; δ(400 MHz) 0.95–1.05 (1 H, m), 1.7–1.95 (2 H, m), 2.49 (1 H, dddd, *J* 14.65, 12.21, 5.37 and 2.93, 6-H), 2.65 (1 H, t, *J* 12.5, 8-H), 3.51 (1 H, dd, *J* 14.65 and 7.81, 6-H), 5.88 (1 H, d, *J* 5.37, 5-H), 6.96 (1 H, d, *J* 7.81), 7.1–7.35 (6 H, m) and 7.99 (1 H, dd, *J* 7.81 and 0.98); *m/z* 252 (M$^+$, 19), and 234 [(M − H$_2$O)$^+$, 100] (Found: C, 88.8; H, 6.25. C$_{17}$H$_{16}$O$_2$ requires C, 80.92; H, 6.39).

6,7-*Dihydro*-7-*iodo*-5H,14H-*benzo*[6,7]*cycloocta*[1,2-a]-*naphthalen*-14-*one* **18** *and* 7,14-*Epoxy*-5,6,7,14-*tetrahydro*-*benzo*[6,7]*cycloocta*[1,2-a]*naphthalen*-14-*ol* **19**.—The photoreaction of the pentacyclic alcohol **9** (60 mg, 0.22 mmol) in benzene (8 cm^3) in the presence of red mercury(II) oxide (143 mg, 0.66 mmol) and iodine (168 mg, 0.66 mmol) for 15 min gave **18** (39 mg, 44%) and **19** (16 mg, 25%): **18** R_F 0.62 (EtOAc–hexane, 1:5); m.p. 147–149 °C (from CH$_2$Cl$_2$–hexane); ν_{max}/cm^{-1} 1648; δ(90 MHz) 2.25–2.55 (4 H, m), 5.40 (1 H, dd, *J* 11.32 and 4.29, 7-H), 7.1–8.0 (9 H, m) and 8.55 (1 H, dd, *J* 7.47 and 1.98, 13-H); *m/z* 399 [(M + 1)$^+$, 0.17], 398 (M$^+$, 0.16) and 271 [(M − I)$^+$, 100] (Found: C, 60.3; H, 3.75. C$_{20}$H$_{15}$IO requires C, 60.32; H, 3.80); **19** R_F 0.23 (EtOAc–hexane, 1:5); m.p. 131–133 °C (from CH$_2$Cl$_2$–hexane); ν_{max}/cm^{-1} 3318; δ(400 MHz) 1.9–2.05 (2 H, m, 6-H), 2.45–2.55 (2 H, m, 5-H), 5.74 (1 H, br s, 7-H), 7.02 (1 H, d, *J* 7.32), 7.13 (1 H, td, *J* 7.3 and 1.46), 7.31 (1 H, dd, *J* 7.82 and 7.32), 7.37 (1 H, d, *J* 8.30), 7.4–7.5 (2 H, m), 7.85–7.9 (1 H, m) and 8.1–8.2 (1 H, m); *m/z* 288 (M$^+$, 74) and 197 (100) (Found: M$^+$, 288.1141. C$_{20}$H$_{16}$O$_2$ requires *M*, 288.1150).

8,15-*Epoxy*-6,7,8,15-*tetrahydro*-5H-*benzo*[7,8]*cyclonona*[1,2-a]*naphthalen*-15-*ol* **20** *and* 3-[3-(2-*Iodophenyl*)*propyl*]*naphtho*-[1,2-c]*furan*-1(3H)-*one* **21**.—The photoreaction of the pentacyclic alcohol **12** (70 mg, 0.25 mmol) in benzene (10 cm^3) in the

presence of red mercury(II) oxide (162 mg, 0.75 mmol) and iodine (191 mg, 0.75 mmol) for 2 h gave **20** (38 mg, 51%) and **21** (17 mg, 16%): **20** R_F 0.36 (EtOAc–hexane, 1:5); m.p. 158–161 °C (from Et$_2$O–hexane); v_{max}/cm^{-1} 3340; δ(400 MHz) 1.8–1.9 (3 H, m), 2.05 (1 H, ddd, J 13.67 and 7.81), 2.35–2.45 (2 H, m), 5.91 (1 H, d, J 8.30, 8-H), 6.93 (1 H, d, J 7.32), 7.18 (1 H, t, J 8.30), 7.3–7.4 (4 H, m), 7.8–7.85 (1 H, m), 7.91 (1 H, d, J 8.30), 7.97 (1 H, d, J 7.32) and 8.37 (1 H, d, J 7.81); m/z 302 (M$^+$, 100) (Found: M$^+$, 302.1324. C$_{21}$H$_{18}$O$_2$ requires M, 302.1307); **21** R_F 0.36 (EtOAc–hexane, 1:5); m.p. 158–161 °C (from Et$_2$O–hexane); v_{max}/cm^{-1} 1748; δ(400 MHz) 1.7–1.95 (3 H, m), 2.15–2.3 (1 H, m), 2.7–2.85 (2 H, m), 5.57 (1 H, dd, J 7.33 and 3.91, 3-H), 6.87 (1 H, ddd, J 7.82, 7.32 and 1.47), 7.18 (1 H, dd, J 7.82 and 1.47), 7.6–7.75 (2 H, m), 7.78 (1 H, dd, J 7.82 and 1.47), 7.96 (1 H, d, J 8.30), 8.12 (1 H, d, J 8.30) and 9.01 (1 H, d, J 8.30, 9-H); m/z 428 (M$^+$, 21), 301 [(M − I)$^+$, 54], 183 [(M − C$_3$H$_6$C$_6$H$_4$I)$^+$, 98] and 155 (100) (Found: C. 58.7; H, 4.15. C$_{21}$H$_{17}$IO$_2$ requires C, 58.90; H, 4.00).

References

1 Previous paper in this series. K. Kobayashi, A. Konishi, Y. Kanno and H. Suginome, *J. Chem. Soc., Perkin Trans. 1*, 1993, 111.
2 *inter alia* (a) H. Suginome and S. Yamada, *J. Org. Chem.*, 1984, **49**, 3753; (b) H. Suginome and S. Yamada, *J. Org. Chem.*, 1985, **50**, 2489; (c) H. Suginom and S. Yamada, *Synthesis*, 1986, 741; (d) H. Suginome, M. Itoh and K. Kobayashi, *J. Chem. Soc., Perkin Trans. 1*, 1988, 491; (e) H. Suginome and S. Yamada, *Tetrahedron*, 1987, **43**, 3371; (f) H. Suginome and S. Yamada, *Tetrahedron Lett.*, 1988, **29**, 79; (g) H. Suginome, M. Itoh and K. Kobayashi, *Chem. Lett.*, 1987, 1527; (h) H. Suginome and S. Yamada, *Chem. Lett.*, 1988, 245; (i) H. Suginome, C. F. Liv, S. Seko, K. Kobayashi and A. Furusaki, *J. Org. Chem.*, 1988, **53**, 5952; (j) H. Suginome, S. Yamada and J. B. Wang, *J. Org. Chem.*, 1990, **55**, 2170; (k) H. Suginome, K. Kobayashi, M. Itoh, S. Seko and A. Furusaki, *J. Org. Chem.*, 1990, **55**, 4933; (l) H. Suginome and J. B. Wang, *Steroids*, 1990, **55**, 353; (m) K.
   Kobayashi, M. Itoh, A. Sasaki and H. Suginome, *Tetrahedron*, 1991, **47**, 5437; (n) K. Kobayashi, A. Sasaki, Y. Kanno and H. Suginome, *Tetrahedron*, 1991, **47**, 7245; (o) K. Orito, K. Yorita and H. Suginome, *Tetrahedron Lett.*, 1991, **32**, 5999; (p) K. Kobayashi, A. Sasaki, H. Takeuchi and H. Suginome, *J. Chem. Soc., Perkin Trans. 1*, 1992, 115; (q) K. Kobayashi, M. Suzuki and H. Suginome, *J. Org. Chem.*, 1992, **57**, 599; (r) H. Suginome, Y. Nakayama and H. Senboku, *J. Chem. Soc., Perkin Trans. 1*, 1992, 1837; (s) H. Suginome and Y. Nakayama, *J. Chem. Soc., Perkin Trans. 1*, 1992, 1843; (t) K. Kobayashi, Y. Kanno, S. Seko and H. Suginome, *J. Chem. Soc., Perkin Trans. 1*, 1992, 3111; (u) H. Suginome and T. Kondoh, *J. Chem. Soc., Perkin Trans. 1*, 1992, 3119.
3 P. Caubere, M. S. Mourad and G. Guillaumet, *Tetrahedron*, 1973, **29**, 1843.
4 G. Adams, J. Andrieux and M. Plat, *Tetrahedron*, 1985, **41**, 399.
5 A. Astier, Thesis, Orsay (1976) cited in ref. 4.
6 J. J. Cornejo, S. Ghodsi, R. D. Johnson, R. Woodling and B. Rickborn, *J. Org. Chem.*, 1983, **48**, 3869.
7 D. W. Hughes, H. L. Holland and D. B. MacLean, *Can. J. Chem.*, 1976, **54**, 2252.
8 L. F. Johnson and W. C. Jankowski, *Carbon-13 NMR Spectra*, Wiley, New York, 1972.
9 P. Caubere, M. S. Mourad and G. Guillaumet, *Tetrahedron*, 1973, **29**, 1851.
10 R. N. Renaud and J. W. Bovenkamp, *Can. J. Chem.*, 1977, **55**, 650.
11 D. C. Remy, P. S. Anderson, M. E. Christy and B. E. Evans, *J. Org. Chem.*, 1978, **43**, 4311.
12 I. Willner and M. Rabinovitz, *Tetrahedron*, 1979, **35**, 2359; I. Willner, A. Minsky and M. Rabinovitz, *J. Org. Chem.*, 1979, **44**, 4440.
13 S. O. Winthrop, M. A. Davis, F. Herr, J. Stewart and R. Gaudry, *J. Med. Chem.*, 1963, **6**, 130; K. Ackermann, J. Chapuis, D. E. Horning, G. Lacasse and J. M. Muchowski, *Can. J. Chem.*, 1969, **47**, 4327; F. E. Elhadi, W. D. Ollis and J. F. Stoddart, *Angew. Chem., Int. Ed. Engl.*, 1976, **15**, 224; T. Eicher, H. Pielartzik and P. Zacheus, *Tetrahedron Lett.*, 1984, **25**, 4495.