

Photoinduced Molecular Transformations. Part 152.¹ Ring Expansion based on a Sensitized [2 + 2] Photoaddition of Enol Ethers of Cyclic Ketones with Olefins, followed by a β -Scission of Alkoxy Radicals generated from the Resulting Cyclobutanols. Two-Carbon Ring Expansion of β -Indanone, β -Tetralone and β -Suberone²

Hiroshi Suginome,* Toshihiro Takeda, Masahito Itoh, Yutaka Nakayama and Kazuhiro Kobayashi
Organic Synthesis Division, Faculty of Engineering, Hokkaido University, Sapporo 060, Japan

A new method for two-carbon ring expansions of the 5-, 6- and 7-membered rings of β -indanone, β -tetralone and β -suberone is described. The sequence involves a sensitized [2 + 2] photoaddition of the trimethylsilyl enol ethers of the cyclic ketones with acrylonitrile or methyl acrylate, followed by a β -scission of the alkoxy radicals generated from the resulting cyclobutanols. The syntheses of functionalized benzocycloheptane, benzocyclooctane and benzocyclononane rings were achieved by this method. The ring expansion of cyclobutanols derived from the [2 + 2] photoaddition of trimethylsilyl enol ethers of β -tetralone and β -indanone with methyl acrylate afforded γ -lactones as by-products, which arose from a transannular bonding of the carbonyl oxygen and the cationic centre of the carbocationic intermediates generated by β -scissions of the alkoxy radicals.

In previous papers³ we have shown that a variety of molecules, including natural products, can be synthesized by methods involving the selective fragmentation of alkoxy radicals, which were generated by photolysis of corresponding hypoiodites, as the key step.⁴ The classes of the molecules synthesized by these methods include heterosteroids,^{3a} 18- and 19-norsteroids,^{3b} steroidal lactones,^{3c} benzohomotropones,^{3d} 18-functional steroids,^{3e} lignans,^{3f} medium-sized lactones,^{3g} macrolides,^{3h} phthalides,³ⁱ naphthalide lignanes,^{3j} monocyclic lactones,^{3k} macrocyclic ketones,^{3l} furanoheterocycles,^{3m,n} furanoquinolones,^{3o} isocoumarins^{3p} and sesquiterpenes.^{3q}

Among these synthetic applications of the β -scission reaction of alkoxy radicals, one of the most useful applications was the synthesis of medium-sized^{3g} and macrocyclic lactones^{3h} and ketones.^{3l} We thus showed that medium-sized lactones and macrolides such as phoracantholide^{3g} and exaltolide^{3h} can generally be synthesized by a regioselective β -scission of the ring-junction bond of the alkoxy radicals generated from bicyclic lactols.^{3g,h} We also showed that macrocyclic ketones such as muscone can generally be synthesized by a similar reaction of the alkoxy radicals generated from catacondensed bicyclic alcohols.^{3l}

The ring-expansion approach to medium and large rings has been a powerful strategy in synthetic organic chemistry, as has been summarized by several excellent reviews.⁵ Most of these ring expansions were, however, achieved by ionic reactions by rather strong acid or base. In contrast, radical fragmentation was seldom used in ring expansions by synthetic organic chemists at the time we initiated the exploratory work mentioned above, despite the advantages of a radical process that can be carried out under virtually neutral conditions.

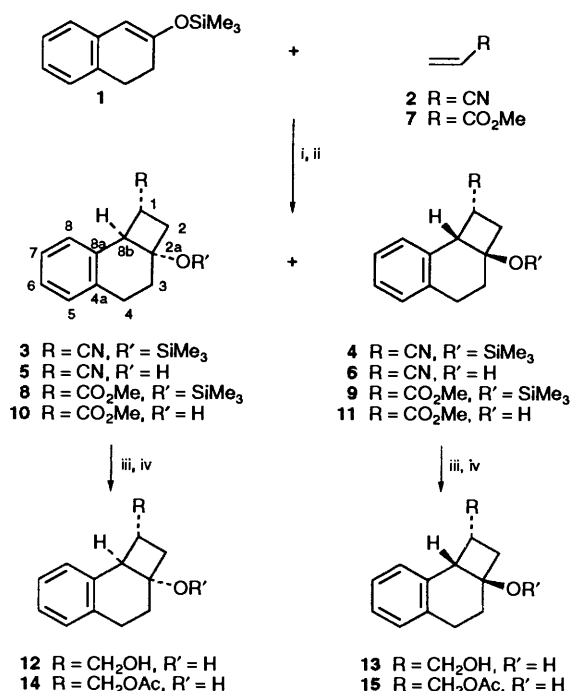
Subsequent to our work, however, an increasing use of the radical process for ring expansion have appeared in the literature and the results were recently summarized.^{5c}

In this paper, we report in full the synthesis of functionalized benzocycloalkanes by a two-carbon ring expansion of benzocycloalkanones. The synthesis involves a sensitized [2 + 2] photoaddition of the enol ethers of benzocycloalkanones with olefins, followed by a selective radical fragmentation of the resulting fused cyclobutanols.² The work was carried out as part of our programme to explore the synthetic potential of the [2 + 2] photoaddition-radical fragmentation sequence.^{3d,m-o,q}

While the two-carbon ring expansion involving the [2 + 2] photoaddition of enolized 1,3-diketones with alkenes-ionic fragmentation sequence^{6,7} and others⁸ has been reported, no two-carbon ring expansion involving radical fragmentation has been reported and the present work represents the first example.

Results

Synthesis of Cyclobutanols 5, 6, 10–15, 19, 20, 25–28, 32 and 33 by [2 + 2] Photocycloaddition of Trimethylsilyl Enol Ethers 1, 16 and 29 of β -Tetralone, β -Indanone and β -Suberone with Acrylonitrile or Methyl Acrylate (Schemes 1–3).—Trimethylsilyl enol ethers 1, 16 and 29 of β -tetralone, β -indanone and β -suber-



Scheme 1 Reagents and conditions: i, hv, benzene, Michler's ketone; ii, HCl-THF, 0 °C; iii, LiAlH₄, Et₂O, 0 °C; iv, AcCl, Et₃N, THF, 0 °C

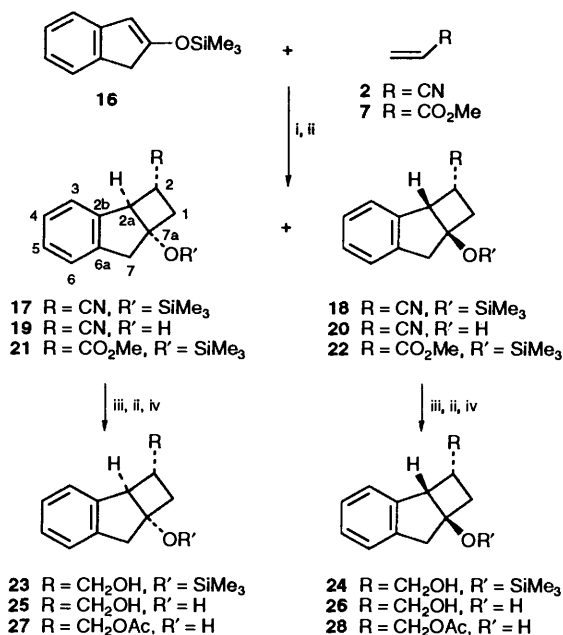
one were prepared in 65–90% yield according to the procedure of House and colleagues.^{8,9}

The triplet-sensitized photocycloaddition of β -tetralone trimethylsilyl enol ether **1** to an excess of acrylonitrile **2** in benzene in the presence of Michler's ketone with Pyrex-filtered light generated by a 500 W high-pressure Hg arc lamp gave a mixture of two stereoisomers of [2 + 2] photoadducts, **3** and **4**, which were separable by preparative TLC (PLC). Treatment of the more mobile isomer **3** dissolved in tetrahydrofuran (THF) with 5 drops of hydrochloric acid at room temperature, followed by the usual work-up, gave a crystalline photoadduct **5** in 32% yield. The structure and stereochemistry were established to be (\pm)-(1 α ,2 $\alpha\alpha$,8 $\beta\alpha$)-2 α -hydroxy-1,2,2 α ,3,4,8 β -hexahydrocyclobuta[*a*]naphthalene-1-carbonitrile on the basis of an analysis of the ¹H NMR spectrum and the nuclear Overhauser enhancement (NOE) results. Details of the analysis of the spectra are described in the Experimental section. An NOE enhancement of the signal area at δ 2.41 (2 α -H) was observed when the signal at δ 3.66 (8 β -H) was irradiated and *vice versa*. A similar acidic hydrolysis of the less mobile isomer **4** gave an oily isomeric adduct **6**, which was purified by distillation (Kugelrohr), in 27% yield. The structure and stereochemistry were again established by ¹H NMR spectroscopy and NOE results; irradiation of the signal at δ 3.67 (8 $\beta\beta$ -H) resulted in an enhancement of the signal area at δ 3.51 (1 β -H), while irradiation at δ 3.51 resulted in an enhancement of the signal area at δ 3.67. These results indicated that 8 β -H and 1-H are *cis*-oriented, and adduct **6** was therefore (\pm)-(1 α ,2 $\alpha\beta$,8 $\beta\beta$)-2 α -hydroxy-1,2,2 α ,3,4,8 β -hexahydrocyclobuta[*a*]naphthalene-1-carbonitrile. A similar triplet-sensitized [2 + 2] cycloaddition of β -tetralone trimethylsilyl enol ether **1** to excess of methyl acrylate **7** in benzene with Pyrex-filtered light, followed by treatment of the stereoisomeric [2 + 2] photoadducts **8** and **9** with hydrochloric acid, gave a mixture of two stereoisomers of the adduct products. Separation of the mixture by PLC gave adducts **10** and **11** in 38 and 35% yield, respectively. The structures of adducts **10** and **11** were established to be (\pm)-(1 α ,2 $\alpha\alpha$,8 $\beta\alpha$)-methyl 2 α -hydroxy-1,2,2 α ,3,4,8 β -hexahydro-2,3-cyclobutanaphthalene-1-carboxylate and its 1 α ,2 $\alpha\beta$,8 $\beta\beta$ -isomer on the basis of analyses of their IR, ¹H NMR, and mass spectra. Full details of the spectral analysis are described in the Experimental section. The spectra of cyclobutanols **10** and **11** showed a singlet (3 H) at δ 3.77 and 3.24 assignable to the CO₂Me groups. A considerable downfield shift of the signal due to the CO₂Me of the cyclobutanol **10**, when compared with the signal position of the CO₂Me of the cyclobutanol **11**, indicated that the CO₂Me and the angular OH are *cis*-oriented in the cyclobutanol **10**, while they are *trans*-oriented in the cyclobutanol **11**.

A reduction of cyclobutanols **10** and **11** in diethyl ether with LiAlH₄ at 0 °C gave the corresponding diols, **12** and **13**, in 82 and 74% yield, respectively. Acetylation of diols **12** and **13** in THF with acetyl chloride in the presence of triethylamine gave the corresponding acetates, **14** and **15**, in 93 and 99% yield, respectively. The results of NOE measurements for the ¹H NMR spectra of these monoacetates were fully consistent with the assigned stereochemistries. Irradiation of the 8 β -H signal of **14** resulted in no enhancement of the signal area of the 1-H signal, and *vice versa*. The results of this NOE indicated that the 8 β -H and CH₂OAc attached to C(1) are *cis*-oriented.

The ¹H NMR spectrum of acetate **15**, on the other hand, showed the angular 8 β -H signal as a doublet at δ 3.57 (*J* 10.23) and the 1-H signal as a multiplet at δ 3.05–3.15. Irradiation of the 8 β -H signal resulted in an enhancement of the signal area of the 1-H signal (13%), while irradiation of the 1-H signal resulted in an enhancement of the 8 β -H signal (14%), indicating a *trans*-orientation of the 8 β -H and CH₂OAc group.

The triplet-sensitized photocycloaddition of β -indanoine

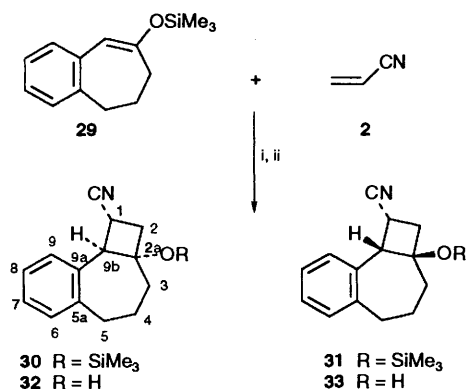


Scheme 2 Reagents and conditions: i, hv, benzene, Michler's ketone; ii, HCl-THF, 0 °C; iii, LiAlH₄, Et₂O, 0 °C; iv, AcCl, Et₃N, THF, 0 °C

trimethylsilyl enol ether **16** and an excess of acrylonitrile **2** in benzene in the presence of Michler's ketone under the same conditions as those applied to the [2 + 2] photocycloaddition of enol ether **1** gave a mixture of photoadducts **17** and **18**. Treatment of the mixture with aq. HCl at 0 °C gave a mixture of cyclobutanols, which was separated to (\pm)-(2 α ,2 $\alpha\alpha$,7 $\alpha\alpha$)-7 α -hydroxy-2,2 α ,7,7 α -tetrahydro-1*H*-cyclobuta[*a*]indene-2-carbonitrile **19** and its 2 α ,2 $\alpha\beta$,7 $\alpha\beta$ -isomer **20** in 51 and 27% yield by means of PLC. Their structures were established by spectroscopy. Details concerning the spectral analysis are described in the Experimental section. The angular 2 α -H and 2-H of adduct **19** should be *trans* oriented, since no enhancement of the signal area due to 2-H was observed when the signal due to 2 α -H was irradiated, and *vice versa*. On the other hand, the *cis* orientation of the angular 2 α -H and 2-H of isomer **20** was confirmed by NOE measurements; irradiation at the signal due to 2 α -H resulted in an enhancement of the signal area due to 2-H, while irradiation of the signal due to 2-H resulted in an enhancement of the signal area due to 2 α -H. Photoaddition of indanone enol ether **16** and an excess of methyl acrylate in benzene in the presence of Michler's ketone under similar conditions also gave a mixture of photoadducts, **21** and **22**. Reduction of the mixture in diethyl ether with LiAlH₄ at 0 °C gave a mixture of primary alcohols, **23** and **24**, a THF solution of which was treated with hydrochloric acid to give a mixture of the cyclobutanols **25** and **26**. Separation of this mixture by PLC gave a crystalline (2 α ,2 $\alpha\alpha$,7 $\alpha\alpha$)-cyclobutanol **25** and a crystalline (2 α ,2 $\alpha\beta$,7 $\alpha\alpha$)-cyclobutanol **26** in 39 and 29% yield (from enol ether **16**), respectively.

Selective partial acetylation of the two cyclobutanol isomers, **25** and **26**, in THF with acetyl chloride in the presence of triethylamine then gave (\pm)-(2 α ,2 $\alpha\alpha$,7 $\alpha\alpha$)-7 α -hydroxy-2,2 α ,7,7 α -tetrahydro-1*H*-cyclobuta[*a*]indene-2-methyl acetate **27** and its (2 α ,2 $\alpha\beta$,7 $\alpha\beta$)-isomer **28** in 97 and 89% yield.

Finally, the triplet-sensitized photocycloaddition of β -suberone trimethylsilyl enol ether **29** and acrylonitrile **2** in a similar manner gave a mixture of photoadducts **30** and **31** in low yield. Acidic hydrolysis of the mixture and subsequent separation of the products by PLC gave the crystalline cyclobutanol **32** and its isomer **33** in 10.1 and 7.1% yield, respectively. Details concerning the analysis of the IR, ¹H

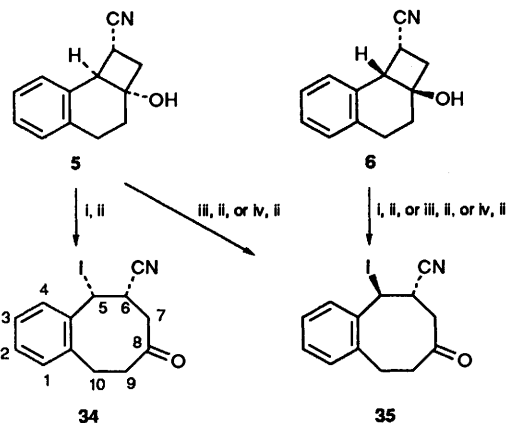


Scheme 3 Reagents and conditions: i, $h\nu$, benzene, Michler's ketone; ii, HCl-THF, 0 °C

NMR and mass spectra of cyclobutanols **32** and **33** are recorded in the Experimental section.

The *trans* and *cis* orientations of the 9b-H and 1-H of cyclobutanols **32** and **33** were established by NOE techniques; irradiation of the 9b-H signal of the cyclobutanol **32** resulted in no enhancement of the 1-H signal and an enhancement of the 2 α -H, while irradiation of the 9b-H signal of the cyclobutanol **33** resulted in an enhancement (8%) of the 1-H signal area.

Functionalized Benzocyclooctanes 34 and 35 by Alkoxy Radical-induced Ring Expansion of Cyclobutanols 5 and 6 formed from a [2 + 2] Photoaddition of Enol Ether 1 of β -Tetralone and Acrylonitrile 2 (Scheme 4).—An alkoxy radical-induced ring expansion was first carried out on cyclobutanols **5** and **6** derived from β -tetralone. Photolysis of the cyclobutanol **5** in benzene containing each 3 mole equivalents of HgO and iodine under nitrogen for 2 h with Pyrex-filtered light gave a single crystalline product **34** in 59% yield. High-resolution mass spectrometry established the molecular formula to be C₁₃H₁₂INO. Spectral analysis, together with the mechanism of its formation, indicated that product **34** was the anticipated 5-iodo-8-oxo-5,6,7,8,9,10-hexahydrobenzo[8]annulene-6-carbonitrile arising from a β -scission of the ring-junction bond of the alkoxy radical generated from the cyclobutanol **5**. The unexpected *cis*-orientation of the iodo and cyano groups was established by NOE measurements; irradiation of the signal at δ 5.18 (5-H) enhanced the area of the signal at δ 3.57 (6 β -H) (14%), and *vice versa*. No interconversion takes place between the isomers **34** and **35** under the above mentioned reaction conditions.



Scheme 4 Reagents and conditions: i, HgO-I₂, benzene; ii, $h\nu$; iii, PhI(OAc)₂-I₂, benzene; iv, Pb(OAc)₄-I₂, benzene

A ring expansion was also carried out with a (diacetoxyiodo)benzene-iodine reagent¹⁰ and with a lead tetra-

acetate-iodine reagent¹¹ in order to confirm whether these hypiodite-generating reagents produce the same results. Thus, the photolysis of the cyclobutanol **5** in benzene containing (diacetoxyiodo)benzene (2 mol equiv.) and iodine (3 mol equiv.) under nitrogen for 2 h with Pyrex-filtered light gave a single crystalline product **35** (41%), which was isomeric with product **34** formed by reaction with HgO-I₂ reagent. The structure was established to be *trans*-5-iodo-8-oxo-5,6,7,8,9,10-hexahydrobenzo[8]annulene-6-carbonitrile on the basis of an analysis of IR and ¹H NMR spectra. The *trans*-orientation of the iodine and cyano groups was assigned on the basis of an NOE measurement. Although irradiation of the doublet at 5.27 (5-H) enhanced the area of the multiplet at δ 3.23–3.5 (6 β -H), and *vice versa*, the enhancements were only 5 and 8%, respectively, which were smaller than those of the *cis*-assigned isomer **34**.

Photolysis of the cyclobutanol **5** in benzene containing lead tetraacetate (3 mol equiv.) and iodine (3 mol equiv.) under nitrogen for 2.5 h with Pyrex-filtered light also gave *trans*-5-iodo-8-oxo-5,6,7,8,9,10-hexahydrobenzo[8]annulene-6-carbonitrile **35** in 54% yield. None of the *cis*-isomer **34** was formed in these ring expansions with (diacetoxyiodo)benzene-iodine or lead tetraacetate-iodine reagents.

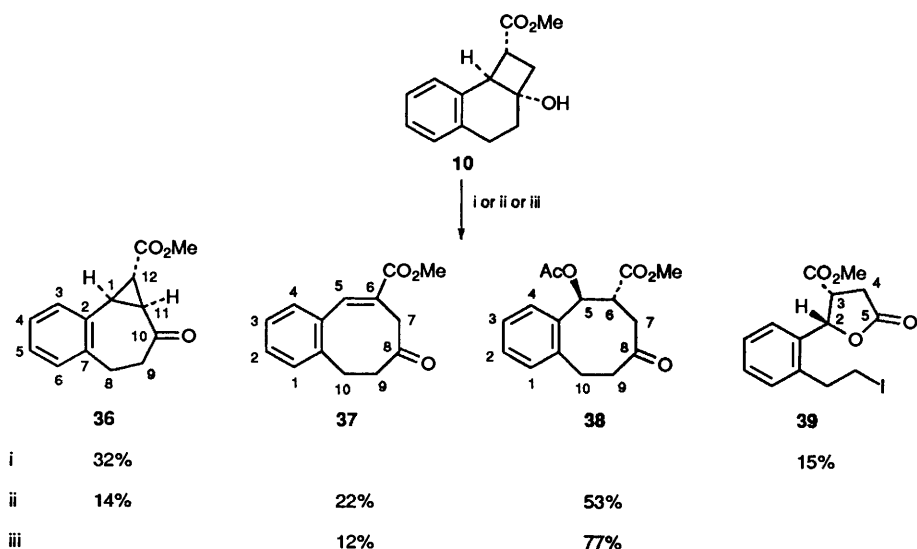
Alkoxy Radical-induced Ring Expansion of Cyclobutanols 10 and 11 formed from a [2 + 2] Photoaddition of Enol Ether 1 of β -Tetralone and Methyl Acrylate 7 (Schemes 5 and 6).—The results of the photolysis of the hypiodite of cyclobutanols **10** and **11** formed *in situ* with the HgO-I₂, (diacetoxyiodo)benzene-I₂ or lead tetraacetate-I₂ reagent in benzene under the same conditions as that of the hypiodites of cyclobutanols **5** and **6** are outlined in Schemes 5 and 6.

Thus, irradiation of the hypiodite of the cyclobutanol **10** generated *in situ* with HgO-I₂ (each 3 mol equiv.) in benzene gave two products, **36** and **39**, in 32 and 15% yield, respectively. The molecular formula of product **36** was established to be C₁₄H₁₄O₃ by high-resolution mass spectrometry. The structure of product **36** was then assigned to be (\pm)-methyl (1 α ,11 α ,12 α)-10-oxotricyclo[9.1.0.0^{2,7}]dodeca-2,4,6-triene-12-carboxylate based on an analysis of the IR, ¹H NMR and mass spectra as well as its mechanism of formation.^{3d} The results of our analysis of the spectra are described in the Experimental section. The coupling constants indicated that 12-H/1-H and 1-H/11-H are both *trans*-oriented (Scheme 5).

The molecular formula of product **39** was established to be C₁₄H₁₅IO₄ by combustion analysis and mass spectrometry. The structure was assigned to be (\pm)-methyl (2 α ,3 α)-2-[2-(2-iodoethyl)phenyl]-5-oxo-tetrahydrofuran-3-carboxylate based on spectroscopic analysis and a consideration of the mechanism of formation (see Experimental section). NOE measurements indicated that irradiation of the signal at δ 5.95 (2 β -H) resulted in an enhancement of the area of the signal at δ 3.70 (3 β -H), and *vice versa*. These experiments indicated that the protons attached to C(2) and C(3) are *cis*-oriented. Irradiation of the signal at δ 3.70 also resulted in an enhancement of the signal area at δ 2.89 assigned to 4 β -H.

Irradiation of the hypiodite of the cyclobutanol **10** generated *in situ* with (diacetoxyiodo)benzene-I₂ (each 4.7 mol equiv.) in benzene gave product **36** (14%) and new products **37** and **38** in 22 and 53% yield, respectively. The molecular formula of product **37** was confirmed to be C₁₄H₁₄O₃ by high-resolution mass spectrometry. An analysis of the IR, ¹H NMR, and mass spectra of product **37**, together with its mechanism of formation, indicated that the product was methyl 8-oxo-7,8,9,10-tetrahydrobenzo[8]annulene-6-carboxylate.

The structure methyl *trans*-5-acetoxy-8-oxo-5,6,7,8,9,10-hexahydrobenzo[8]annulene-6-carboxylate was assigned to product **38** on the basis of an analysis of the IR and ¹H NMR



Scheme 5 Reagents and conditions: i, HgO-I_2 , benzene, $h\nu$; ii, $\text{PhI(OAc)}_2\text{-I}_2$, benzene, $h\nu$; iii, $\text{Pb(OAc)}_4\text{-I}_2$, benzene, $h\nu$

spectra, details of which are described in the Experimental section.

The *trans* orientation of the substituents attached to the benzo[8]annulene **38** was supported by NOE results; irradiation of the doublet due to $5\alpha\text{-H}$ at δ 6.17 resulted in no enhancement of the area of the signal due to $6\beta\text{-H}$ at δ 2.89, and *vice versa*.

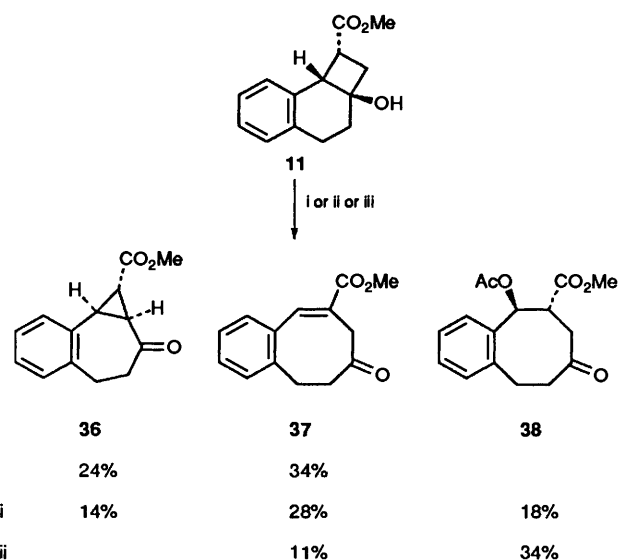
A ring expansion of the cyclobutanol **10** was finally carried out in the presence of a lead tetraacetate–iodine reagent for generating the corresponding hypoiodite. Thus, the major product in this ring expansion was the benzo[8]annulene **38** in 77% yield. In addition to product **38**, the benzo[8]annulene **37** was obtained as a minor product in 12% yield. No products **36** and **39** were formed in this ring expansion (Scheme 5).

A series of ring-expansion reactions was carried out for the cyclobutanol isomer **11**; the results are summarized in Scheme 6. It is notable that both the products and the yields obtained in the photolysis of the hypoiodite generated from the cyclobutanol **10** by the HgO-I_2 reagent substantially differ from those obtained in the corresponding photolysis of the hypoiodite generated from the isomer **11**. None of the γ -lactone **39** was formed, while the benzo[8]annulene **37** was formed together with product **36** as in the reaction of isomer **10**.

In contrast, the photolysis of cyclobutanols **10** and **11** in the presence of $\text{PhI(OAc)}_2\text{-I}_2$ or $\text{Pb(OAc)}_4\text{-I}_2$ afforded the same products, though the yields of compound **38** from isomer **10** were appreciably higher than were those from isomer **11**.

Alkoxy Radical-induced Ring Expansion of Cyclobutanols 14 and 15. (Scheme 7).—A ring expansion through β -scission of the alkoxy radicals generated from photolysis of the hypoiodites derived from the reaction of cyclobutanols **14** and **15** with red mercury(II) oxide–iodine gave the same two products, **40** and **41**, in similar yields (16 and 31%; 24 and 31%).

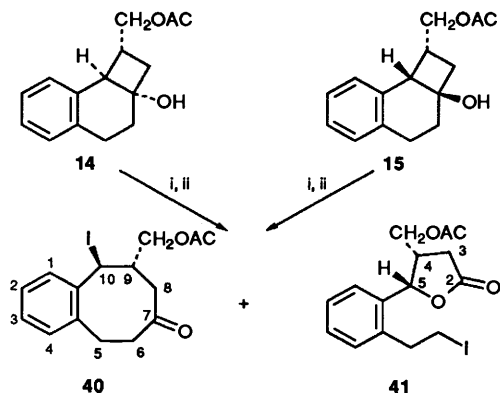
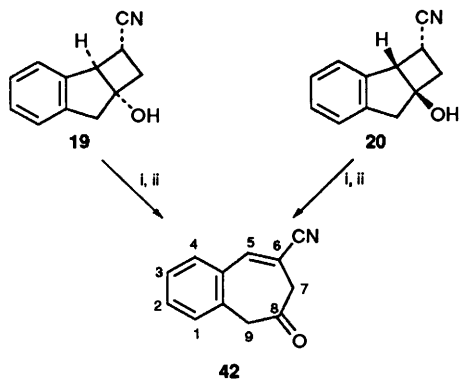
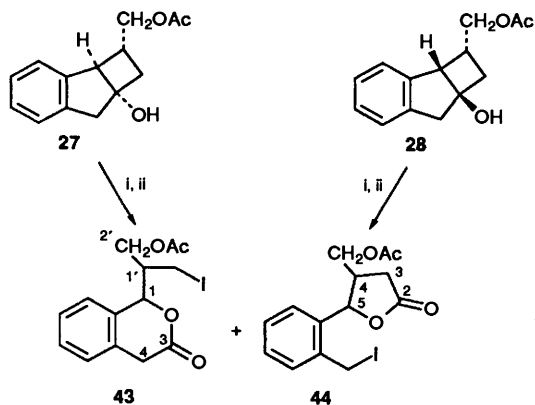
The molecular formula of product **40** was established to be $\text{C}_{15}\text{H}_{17}\text{IO}_3$ by high-resolution mass spectrometry. The results of the spectra, together with the mechanism of formation, indicated that product **40** was 9-[(acetoxy)methyl]-10-iodo-5,6,7,8,9,10-hexahydrobenzo[8]annulene. The *trans* orientation of 10-H and 9-H was indicated by NOE studies; irradiation of the signal at δ 5.46 (10 α -H) resulted in no enhancement of the area of the multiplet at δ 2.3–2.5 (9 β -H), and *vice versa*. The molecular formula of product **41** was established to be



Scheme 6 Reagents and conditions: i, HgO-I_2 , benzene, $h\nu$; ii, $\text{PhI(OAc)}_2\text{-I}_2$, benzene, $h\nu$; iii, $\text{Pb(OAc)}_4\text{-I}_2$, benzene, $h\nu$

$\text{C}_{15}\text{H}_{17}\text{IO}_4$ by high-resolution mass spectrometry. The structure 4-[(acetoxy)methyl]-5-[2-(2-iodoethyl)phenyl]tetrahydrofuran-2-one was assigned to product **41** on the basis of its IR and ^1H NMR spectra as well as its mechanism of formation (*vide infra*). The NOE measurements confirmed that 4-H and 5-H of γ -lactone **41** was *cis*-oriented; irradiation of the doublet at δ 5.88 (5 β -H) resulted in an enhancement of the signal due to 4-H, and irradiation of the multiplet at δ 3.11–3.23 (4 β -H) resulted in an enhancement of the signals at δ 5.88 (5 β -H) and 2.96 (3 β -H).

Ring Expansion of Cyclobutanols 19 and 20 via a β -Scission of the Alkoxy Radicals (Scheme 8).—Generation of the alkoxy radicals from cyclobutanols **19** and its isomer **20** by photolysis of the corresponding hypoiodites [generated *in situ* by HgO-I_2 reagent] gave same principal product **42** in 20 and 28% yield. The molecular formula of product **42** was established to be $\text{C}_{12}\text{H}_9\text{NO}$ by combustion analysis and mass spectrometry. The IR and ^1H NMR spectra indicated that it was 8-oxo-8,9-dihydro-7H-benzo[7]annulene-6-carbonitrile.

Scheme 7 Reagents and conditions: i, HgO-I₂, benzene; ii, hvScheme 8 Reagents and conditions: i, HgO-I₂, benzene; ii, hvScheme 9 Reagents and conditions: i, HgO-I₂, benzene; ii, hv

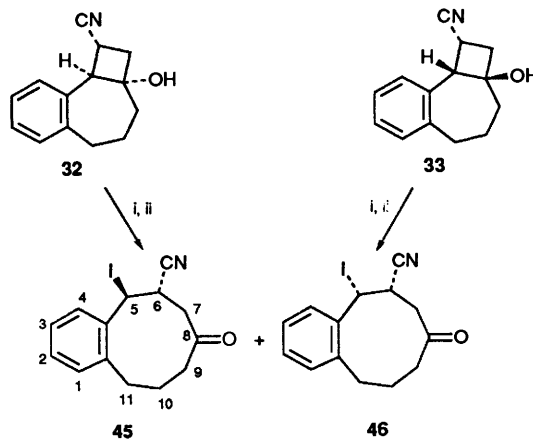
Alkoxy Radical-induced Reactions of Cyclobutanols 27 and 28 (Scheme 9).—Generation of the alkoxy radicals from the cyclobutanol 27 and its isomer 28 by photolysis of the corresponding hypoiodites generated by the HgO-I₂ reagent gave none of the products arising from ring expansion, but gave nearly the same product mixture from which δ -lactone 43 and γ -lactone 44 were obtained in low yields (15 and 7%; 12 and 6%). High-resolution mass spectrometry indicated the isomers had the molecular formulae C₁₄H₁₅IO₄. The spectral analysis indicated that product 43 was a mixture of *cis* and *trans* isomers of 1-[2-acetoxy-2-(iodomethyl)ethyl]-3,4-dihydro-1*H*-2-benzopyran-3-one. The details of the analysis are described in the Experimental section.

The molecular formula of γ -lactone 44 was also established to be C₁₄H₁₅IO₄ by high-resolution mass spectrometry. The IR and ¹H NMR spectra, together with the mechanism of formation, suggested that product 44 was 4-acetoxymethyl-5-[2-(iodomethyl)phenyl]tetrahydrofuran-2-one.

Similar results were obtained in the photolysis of the

hypoiodite of the isomeric cyclobutanol 28 to give δ -lactone 43 and γ -lactone 44 in 12 and 6% yield.

Alkoxy Radical-induced Ring Expansion of Cyclobutanols 32 and 33 (Scheme 10).—Photolysis of the hypoiodite generated from the reaction of the cyclobutanol 32 with HgO-I₂ gave two products, 45 and 46, in 85 and 12% yield. Spectral analysis indicated that the products were isomers arising from the expected ring expansion (Scheme 10). Thus, high-resolution

Scheme 10 Reagents and conditions: i, HgO-I₂, benzene; ii, hv

mass spectrometry established their molecular formula to be C₁₄H₁₄INO. The IR spectra of both products indicated the presence of a nitrile and an unstrained carbonyl group. The ¹H NMR spectrum of both products 45 and 46 exhibited two signals ascribable to the CHI and CHCN groups. Details concerning the analysis of the signals are described in the Experimental section.

The stereochemistries of products 45 and 46 were determined by NOE measurements. Thus, irradiation of a doublet at δ 5.47 due to 5-H in the spectrum of product 46 resulted in an enhancement (17%) of the signal area at δ 3.95 due to 6-H, while irradiation of the signal at δ 3.95 resulted in an enhancement (8%) of the signal area at δ 5.47. These results indicated that the iodo and cyano groups attached to the 9-membered ring of product 46 are *cis*-oriented.

Similar NOE measurements confirmed that the iodo and cyano groups of product 45 are *trans* oriented; no enhancement of the signal area at δ 3.63 (6 β -H) in the ¹H NMR of product 45 was observed when the doublet at δ 5.61 (5 α -H) was irradiated, and *vice versa*.

Discussion

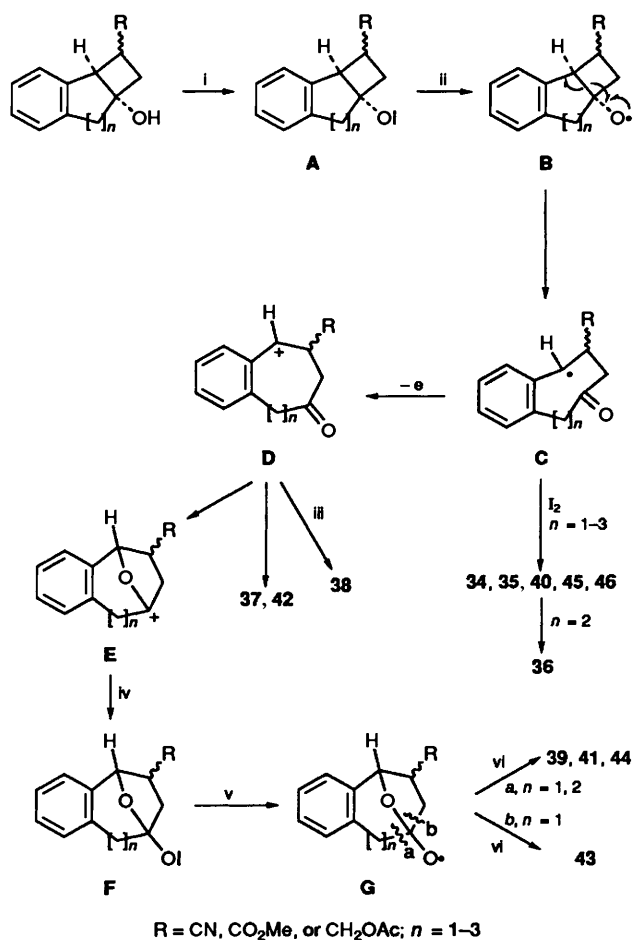
A series of experiments described in the foregoing part indicated that the synthesis of functionalized benzo[7]-benzo[8]- and benzo[9]-annulenes can be achieved by a sequence involving a sensitized [2 + 2] photoaddition of trimethylsilyl enol ethers of β -indanone, β -tetralone, and β -suberone with acrylonitrile or methyl acrylate, followed by a selective β -scission of the alkoxy radicals generated from the resulting cyclobutanols. In the following part, the pathways leading to all of the products arising from a β -cleavage of the alkoxy radicals and some notable features involved in the present results concerning the ring expansion are discussed.

Sensitized [2 + 2] Photoaddition of Trimethylsilyl Enol Ethers 1, 16, and 29 of Benzocycloalkanones with Acrylonitrile or Methyl Acrylate.—The above mentioned experiments have shown that [2 + 2] photoadducts are formed in 59–73% yield by the photoaddition of trimethylsilyl enol ethers of β -indanone

and β -tetralone with acrylonitrile and methyl acrylate, while [2 + 2] photoadducts are formed in a considerably lower yield (17%) in the photoaddition of the trimethylsilyl enol ether of β -suberone with acrylonitrile. The low yield of the [2 + 2] photoadducts in the latter photoaddition can be attributed to the inefficiency of the addition due to a dissipation of excitation energy by $E \rightarrow Z$ isomerization of the double bond.

It is notable that these photoadditions are completely regioselective and gave head-to-tail adducts without exception. These cycloadducts are those expected for the formation of adducts upon the closure of the most stabilized 1,4-biradical with the regiochemistry that parallels the reported triplet-sensitized cycloaddition of indene and acrylonitrile.^{12,13} The aforementioned photoaddition has also produced substantial quantities of sterically less favoured isomers with *cis* substituents attached to C(1) and C(2a), such as **3**, **8**, **17**, **21** and **30** (*cis*-to-*trans* ratio 1:0.52–0.92).¹⁴

Paths leading to Products 34–46 arising from a β -Scission of the Alkoxy Radicals generated from Cyclobutanols 5, 6, 10, 11, 14, 15, 19, 20, 27, 28, 32 and 33 (Scheme 11).—The experiments



Scheme 11 Reagents and conditions: i, I₂O, benzene; ii, benzene, hv; iii, –OAc; iv, I₂O; v, hv; vi, I₂

described above have shown that a β -scission of the alkoxy radicals generated from all of the cyclobutanols prepared in the present work took place exclusively at the ring-junction bonds to give the corresponding ring-expansion product (**34–38**, **40**, **42**, **45** and **46**) and/or lactone (**41**, **43** and **44**).

The probable paths leading to all of these products are summarized in Scheme 11. Thus, photolysis of the hypiodites **A** generated *in situ* by the reaction of cyclobutanols with HgO–I₂, PhI(OAc)₂ or Pb(OAc)₄–I₂ reagent generates alkoxy

radicals **B**. A β -scission selectively at the ring-junction bond then takes place to give a 7- to 9-membered cyclic carbon-centred radical **C**.^{3a} Abstraction of an iodine atom by radical **C** gives rise to iodides **34**, **35**, **40**, **45** and **46**, while a one-electron oxidation of the carbon-centred radical **C**, followed by removal of a proton, gives unsaturated cyclic ketones **37** and **42**. An alternative pathway for the formation of unsaturated cyclic ketones **37** and **42** *via* an elimination of HI from the corresponding iodides is excluded since the iodide is transformed into the corresponding cyclopropane such as **36** rather than the olefin under the experimental conditions. We have already reported analogous cases.^{3d} The acetate **38**, a major product in the photolysis of the hypiodite of cyclobutanols **10** and **11** when PhI(OAc)₂ or Pb(OAc)₄–I₂ reagent is used to generate the hypiodites, should be produced by a reaction of carbocation **D** with acetic acid present in the solution.

By-products, such as δ -lactone **43**, or γ -lactones, such as **39**, **41** and **44**, are also formed from carbocation **D**. Thus, a transannular reaction of the carbonyl oxygen of the intermediate **D** gives epoxide carbocation **E**, which reacts with I₂O to give a second hypiodite **F**. The observed δ -lactone **43** or γ -lactones **39**, **41** and **44** are formed *via* a β -scission of the carbon–carbon bond (*a* or *b*) of the alkoxy radical **G** generated under the photolysis conditions as outlined in Scheme 11. The first example of this reaction was found by us in the photolysis of a steroidal alcohol hypiodite.^{3a,15} The mechanism of the reaction (outlined in Scheme 11) was confirmed by us on the basis of ¹⁸O-labelling experiments with ¹⁸O-labelled mercury(II) oxide as the source of I₂¹⁸O.^{3a,16} Since then, a number of additional examples of this process have been found by us.^{3i–k,17}

The results presented in the foregoing part indicate several interesting features concerning the effects of the ring size, the substituents attached to the four-membered ring, and the reagents for generating the hypiodites in this alkoxy radical-induced ring expansion process. We now briefly present some notable features on the scope and limitation of the ring expansion.

Effects of Ring Size.—The foregoing results indicated that the β -scission of the alkoxy radicals, generated from all the bicyclic alcohols mentioned above, took place selectively at the ring-junction bond without exception. The results also indicated that the ring expansion can be most successfully achieved with bicyclic alcohols derived from β -tetralone and β -suberone, while those derived from β -indanone mostly resulted in products derived from the secondary transannular reaction of the first formed cyclic carbon-centred radicals **C** (*e.g.*, Scheme 9). The results indicate that the carbonyl oxygen and the carbon-centred radical are appropriately located for a transannular reaction in the 7-membered cyclic radicals **C** (*n* = 1) outlined in Scheme 11.

Effects of Substituents attached to the Four-membered Ring.—The aforementioned results showed that substituents attached to the four-membered ring of the cyclobutanols appreciably affect the yields and structures of the products. Thus, the results outlined in Schemes 4, 8 and 10 indicate that the photoreaction of bicyclic alcohol hypiodites derived from the photoaddition of enol ethers of the cyclic ketones with acrylonitrile generally results in clean products arising from a ring expansion, while those derived from the photoaddition of enol ethers of cyclic ketones with methyl acrylate resulted in several products, including those derived from secondary reactions of the first-formed cyclic carbon-centred radicals **C** (Scheme 11). The more enolizable character of the methoxycarbonyl group may

play a role in these product differences, although the exact mechanism is obscure at present.

Stereochemistry of the Formation of Iodides 34, 35, 40, 45 and 46 from the Cyclic Carbon-centred Radical C (Scheme 11).—Photolysis of the hypoiodite of the cyclobutanol **5** generated by mercury(II) oxide–iodine reagent gave exclusively 5-iodo-8-oxo-5,6,7,8,9,10-hexahydrobenzo[8]annulene-6-carbonitrile **34** having *cis*-oriented iodine and cyano groups, whereas photolysis of the hypoiodite of the isomeric cyclobutanol **6** gave the corresponding benzo[8]annulene **35** having *trans*-oriented iodine and cyano groups.

The formation of the stereoisomer **34** from the cyclobutanol **5** and of isomer **35** from the cyclobutanol **6** is remarkable, since products **34** and **35** are regarded as being formed from a common radical intermediate **C**. These results, however, may be explained by assuming that the reaction is a heterogeneous one; the hypoiodite of the cyclobutanol **5** is adsorbed on the surface of HgO *via* its less hindered β -face, and, therefore, the iodine would approach from the α -face of the cyclic radical **C** to give α -iodide **34**.

On the other hand, photolysis of the hypoiodites of cyclobutanols **5** and **6** generated either by (diacetoxyiodo)benzene–iodine reagent or by lead tetraacetate–iodine reagent gave the same iodide **35** having *trans*-oriented iodine and cyano groups. These results indicate that, in contrast to the reaction with the above mentioned mercury(II) oxide–iodine, this type of reaction is a homogeneous one, and, thus, the incoming bulky iodine approaches the carbon-centred radical **C** (Scheme 11) from side *trans* to the cyano group to give iodide **35**.

Effects of the Hypoiodite-generating Reagents on the Type of Products in the Ring Expansion Reactions.—The aforementioned experiments disclosed that the acetoxy group is introduced when the hypoiodites of cyclobutanols **10** and **11** generated from the corresponding alcohols and (diacetoxyiodo)benzene– or lead tetraacetate–iodine reagent are photolysed. It is apparent that these products are formed by the reaction of cyclic carbocation **D** and acetic acid present in the solution. The incorporation of the acetoxy group into the reaction products may or may not be a disadvantage when this ring expansion is used in organic synthesis.

Conclusions.—As mentioned at the outset of this paper, ring expansions *via* [2 + 2] photoaddition–ionic fragmentation^{6,7} are usually carried out under rather strong basic or acidic conditions. Moreover, they require an extra functional group attached to the substrates for the fragmentation to occur. The results described above have shown that a radical-induced ring expansion takes place under virtually neutral conditions and that no extra functional group attached to the substrate is necessary for regioselective cleavage to occur. The complete regioselectivity shown in the [2 + 2] photoaddition of the enol ethers of benzocycloalkanones with methyl acrylate or acrylonitrile may offer another advantage in synthesis of compounds of this type.

Experimental

M.p.s were recorded with a Yanagimoto melting-point apparatus and are uncorrected. IR spectra were determined for Nujol mulls unless stated otherwise with a Hitachi Model 285 infrared spectrometer or a JASCO IR-810 spectrometer. ¹H NMR spectra were determined in CDCl₃, with SiMe₄ as internal reference, with a JEOL JNM-FX 270 FT or a JEOL JNM-GX 270 FT NMR spectrometer operating at 270 MHz. *J*-Values are given in Hz. High- and low-resolution mass spectra

were recorded with a JEOL JMS-D300 (70 eV) or a JMS-DX 303 spectrometer. PLC was carried out on Merck Kieselgel 60PF₂₅₄. Photocycloadditions were carried out with a 500 W high-pressure Hg arc lamp (EIKOSHA, PIH-500S-HPL-3). Photolysis of hypoiodites were carried out with a 100 W high-pressure Hg arc lamp (EIKOSHA, PIH-100).

β -Tetralone Trimethylsilyl Enol Ether 1.—To a solution of β -tetralone (2.4 cm³; 18.2 mmol) and triethylamine (10 cm³, 71.7 mmol) in dimethyl sulfoxide (DMSO) (12 cm³) was added trimethylsilyl chloride (4.6 cm³, 36.2 mmol). The solution was stirred for 5 days at room temperature under nitrogen, and was then filtered. The filtrate was washed with water. The water layer was extracted with hexane. The combined organic layers were washed successively with 5% aq. sodium hydrogen carbonate and dil. hydrochloric acid (to pH 3, by universal indicator). The solution was then washed successively with water and brine, and dried over anhydrous sodium sulfate. Removal of the solvent gave crude, thick, yellow, oily trimethylsilyl enol ether **1** (3.58 g, 90%). This crude product contained 5% of the starting material (¹H NMR) and was purified by distillation; b.p. 120–128 °C (16 mmHg); δ_{H} 0.26 (9 H, s, SiMe₃), 2.34 (2 H, t, *J* 8.25), 2.28 (2 H, t, *J* 8.25), 5.68 (2 H, s) and 6.78–7.08 (4 H, m). This was immediately subjected to photoaddition.

β -Indanone Trimethylsilyl Enol Ether 16.—To a solution of β -indanone (2 g, 15.2 mmol) and triethylamine (8.4 cm³, 60.4 mmol) in DMSO (10 cm³) was added trimethylsilyl chloride (3.9 cm³, 30.3 mmol). The solution was stirred for 3 days under nitrogen, and was then filtered. The filtrate was washed with water. The washings were extracted with hexane. The hexane layer was combined with the organic layer. The solution was worked up as described above to give crude, oily, trimethylsilyl enol ether **16** (2.40 g, 77%), δ_{H} 0.31 (9 H, s, SiMe₃), 3.30 (2 H, s), 5.76 (1 H, s) and 7.08–7.28 (4 H, m). This crude product contained ~5% of the β -indanone but was immediately subjected to photoaddition.

β -Suberone Trimethylsilyl Enol Ether 29.—To a solution of β -suberone (1.93 g, 12.1 mmol) and triethylamine (6.7 cm³, 48.3 mmol) in dry DMSO (8.4 cm³) was added trimethylsilyl chloride (3.1 cm³, 24.2 mmol). The solution was stirred for 28 h at room temperature under nitrogen, and was then filtered. The filtrate was washed with water. The aqueous layer was extracted with hexane. The hexane layer was combined with the filtrate. The solution was worked up as described for the preparation of β -tetralone trimethylsilyl enol ether **1** to give an oily product, which was subjected to column chromatography (Florisil, hexane as eluent) to give the title trimethylsilyl enol ether **29** (1.825 g, 65%), $\nu_{\text{max}}/\text{cm}^{-1}$ 1647, 1152 and 844; δ_{H} (270 MHz) 0.27 (9 H, s), 1.87–1.96 (2 H, m), 2.43 (2 H, t, *J* 6.60), 2.79 (2 H, t, *J* 6.60), 2.79 (2 H, t, *J* 5.28), 5.90 (1 H, s), 7.01–7.04 (3 H, m) and 7.09–7.15 (1 H, m) (Found: M⁺, 232.1268. C₁₄H₂₀OSi requires M, 232.1283).

Photocycloaddition of 3-Trimethylsiloxy-1,2-dihydronaphthalene 1 with Acrylonitrile 2.—A solution of trimethylsilyl enol ether **1** (1 g, 4.6 mmol), acrylonitrile **2** (3.2 g, 60.8 mmol), and Michler's ketone (0.37 mmol) in benzene (35 cm³) was irradiated, with Pyrex-filtered light generated with a 500 W high-pressure mercury arc lamp, for 18 h under nitrogen. The solution was then filtered through Celite, and the solvent was removed by a rotary evaporator. The oily product was distilled using a Kugelrohr (120 °C/0.2 mmHg, bath temp.) to give a crude mixture of the stereoisomers of the photoadduct (1.04 g). The mixture was subjected to PLC (1 : 5 EtOAc–hexane) to give two fractions (A and B). Each fraction was treated with

hydrochloric acid in THF (5 cm³) (5 drops) for 30 min at room temperature, and was then extracted with diethyl ether. The extract was washed successively with aq. sodium hydrogen carbonate and water, and was dried over anhydrous magnesium sulfate. Removal of the solvent from the filtered solution gave an oily product. The less polar adduct was subjected to PLC (1:3 ethyl acetate–hexane, *R_f* 0.30) to give (±)-(1 α ,2 α ,8 β α)-2 α -hydroxy-1,2,2a,3,4,8b-hexahydrocyclobuta[a]naphthalene-1-carbonitrile **5** (297 mg, 32% from **1**), m.p. 109–110 °C (from diethyl ether–hexane); ν_{\max} (neat)/cm⁻¹ 3490 (OH) and 2245 (CN); δ_{H} (270 MHz) 1.80 (1 H, ddd, *J* 12.92, 11.73 and 4.03, 3-H), 1.98 (1 H, ddd, *J* 12.92, 4.40 and 1.10, 3-H), 2.10 (1 H, s, OH), 2.43–2.55 (2 H, m, 1 β - and 2 β -H), 2.41 (1 H, dd, *J* 10.23 and 7.92, 2 α -H), 2.67 (1 H, dt, *J* 16.11 and 4.40, 4-H), 2.90 (1 H, ddd, *J* 16.11, 11.73 and 4.03, 4-H), 3.66 (1 H, d, *J* 8.41, 8b-H) and 7.15–7.25 (4 H, m, ArH); *m/z* 199 (M⁺, 0.7) and 146 [(M – CH₂=CHCN)⁺, 100%] (Found: C, 78.5; H, 6.7; N, 7.2. C₁₃H₁₃NO requires C, 78.37; H, 6.57; N, 7.03%).

The polar isomer **6** was distilled by Kugelrohr distillation [150 °C (bath temp.), 0.1 mmHg] to afford the (1 α ,2 α β ,8 β β)-isomer (242 mg, 27% from **1**), ν_{\max} (neat)/cm⁻¹ 3400 (OH) and 2230 (CN); δ_{H} (270 MHz) 1.91 (1 H, dddd, *J* 9.53, 7.69, 4.77 and 0.73, 3-H), 2.09 (1 H, ddd, *J* 9.53, 9.16 and 5.13, 3-H), 2.15 (1 H, s, OH), 2.41 (1 H, ddd, *J* 12.46, 4.40 and 0.73, 2 α -H), 2.54 (1 H, ddd, *J* 12.46, 9.89 and 0.73, 2 β -H), 2.75–2.95 (2 H, m, 4-H), 3.51 (1 H, td, *J* 9.89 and 4.40, 1 β -H), 3.67 (1 H, d, *J* 9.89, 8b-H), 7.0–7.05 (1 H, m, ArH) and 7.15–7.25 (3 H, m, ArH); *m/z* 199 (M⁺, 0.6) and 146 [(M – CH₂=CHCN)⁺, 100%] (Found: M⁺, 199.1022. C₁₃H₁₃NO requires M, 199.0997).

Photocycloaddition of 3-Trimethylsiloxy-1,2-dihydronaphthalene 1 with Methyl Acrylate 7.—A solution of trimethylsilyl enol ether **1** (1.0 g, 4.58 mmol) and methyl acrylate **7** (5.2 cm³, 57.7 mmol) in benzene (35 cm³) containing Michler's ketone (150 mg) was flushed with nitrogen and irradiated for 23 h with Pyrex-filtered light generated from 500 W high-pressure Hg arc lamp. Removal of the solvent by a rotary evaporator gave an oily product, which was dissolved in THF (7 cm³). To this solution at 0 °C was added conc. hydrochloric acid (5 drops); the solution was stirred for 30 min, and was then poured into water. The aqueous mixture was extracted with diethyl ether. The extract was washed successively with 5% aq. sodium hydrogen carbonate, water and brine, and was then dried over anhydrous sodium sulfate. Evaporation of the solvent gave a viscous oil (1.394 g), which was subjected to PLC (1:3 THF–hexane), to give (±)-methyl (1 α ,2 α ,8 β α)-2 α -hydroxy-1,2,2a,3,4,8b-hexahydrocyclobuta[a]naphthalene-1-carboxylate **10** (404 mg, 38% from **1**) and its 1 α ,2 α β ,8 β β -isomer **11** (375 mg, 35% from **1**).

Adduct **10**, m.p. 112–113 °C (from diethyl ether–hexane); *R_f* 0.36 (1:3 THF–hexane); ν_{\max} (neat)/cm⁻¹ 3450 (OH) and 1710 (CO₂Me); δ_{H} 1.8 (1 H, ddd, *J* 13.6, 11.5 and 4.13, 3-H), 1.99 (1 H, td, *J* 13.5 and 3.96, 3-H), 2.39 (1 H, s, *J* 7.92, OH), 2.32–2.54 (2 H, m, 1 β - and 2 β -H), 2.53 (1 H, dd, *J* 8.91 and 1.92, 2 α -H), 2.67 (1 H, td, *J* 16.2 and 4.29, 4-H), 2.92 (1 H, ddd, *J* 15.8, 11.7 and 3.97, 4-H), 3.54 (1 H, d, *J* 7.92, 8b α -H), 3.77 (3 H, s, OMe) and 7.14 (4 H, m, ArH); *m/z* 232 (M⁺, 8.7) and 146 [(M – CH₂=CHCO₂Me)⁺, 100%] (Found: C, 72.4; H, 7.05. C₁₄H₁₆O₃ requires C, 72.39; H, 6.94%).

Adduct **11**, *R_f* 0.27 (1:3 THF–hexane); ν_{\max} (neat)/cm⁻¹ 3450 (OH) and 1718 (CO₂Me); δ_{H} (270 MHz) 1.69 (1 H, ddd, *J* 13.2, 4.62 and 8.58, 3-H), 1.93 (1 H, s, OH), 2.15 (1 H, ddd, *J* 13.2, 7.25 and 4.62, 3-H), 2.23 (1 H, ddd, *J* 13.2, 9.57 and 2.31, 2 β -H), 2.68 (1 H, dd, *J* 13.2 and 5.94, 2 α -H), 2.73–2.93 (2 H, m, 4-H₂), 3.24 (3 H, s, OMe), 3.67 (1 H, ddd, *J* 11.22, 9.57 and 5.94, 1 β -H), 3.75 [1 H, dd, *J* 11.22 and 2.31 (W-coupling), 8b β -H], 6.98–7.03 (1 H, m, ArH) and 7.03–7.14 (3 H, m, ArH); *m/z* 232 (M⁺, 10.5) and 146 [(M – CH₂=CHCO₂Me)⁺, 100%] (Found: M⁺, 232.1109. C₁₄H₁₆O₃ requires M, 232.1100).

(±)-1 α ,2 α ,8 β α -2 α -Hydroxy-1,2,2a,3,4,8b-hexahydrocyclobuta[a]naphthalene-1-methanol **12.**—To a stirred suspension of LiAlH₄ (35 mg, 0.93 mmol) in dry diethyl ether (3 cm³) at 0 °C was added dropwise a solution of the [2 + 2] cycloadduct **10** (217 mg, 0.93 mmol) in diethyl ether (3 cm³). The solution was stirred for 2 h and was then diluted with diethyl ether. To the solution was added dropwise saturated aq. sodium thiosulfate. The solution was poured into water and the reaction mixture was extracted with diethyl ether. The extract was washed successively with water and brine and dried over anhydrous Na₂SO₄. Removal of the solvent gave crude, oily diol **12**, which was subjected to PLC (1:1 ethyl acetate–hexane) to give pure diol **12** (156 mg, 82%), ν_{\max} (neat)/cm⁻¹ 3256 (OH) and 742; δ_{H} (270 MHz) 1.82–1.91 (3 H, m, 1 β -H and 3-H₂), 1.98 (1 H, dd, *J* 11 and 8.58, 2 β -H), 2.20 (1 H, dd, *J* 11 and 8.25, 2 α -H), 2.34 (2 H, s, OH), 2.67 (1 H, td, *J* 16.16 and 4.95, 4-H), 2.83–2.94 (1 H, m, 4-H), 3.13 (1 H, d, *J* 11.758, 8b α -H), 3.81 (2 H, d, *J* 5.28, CH₂OH) and 7.06–7.16 (4 H, m, ArH); *m/z* 204 (M⁺, 1.1), 186 [(M – H₂O)⁺, 11.8] and 146 [(M – CH₂=CHCH₂OH)⁺, 100%] (Found: M⁺, 204.1137. C₁₃H₁₆O₂ requires M, 204.1150).

(±)-(1 α ,2 α β ,8 β β)-2 α -Hydroxy-1,2,2a,3,4,8b-hexahydrocyclobuta[a]naphthalene-1-methanol **13.**—The [2 + 2] cycloadduct **11** (43 mg, 0.185 mmol) in diethyl ether (2 cm³) was reduced with LiAlH₄ (8.4 mg, 0.22 mmol) in dry diethyl ether (2 cm³), as described for the reduction of *cis,cis*-isomer **10**. The product was subjected to PLC (1:1 ethyl acetate–hexane) to give the *cis,trans*-isomer **13** (28 mg, 74%), ν_{\max} (neat)/cm⁻¹ 3212 (OH) and 744; δ_{H} (270 MHz) 1.66 (2 H, s, OH), 1.73 (1 H, ddd, *J* 13.53, 8.57 and 4.95, 3-H), 1.89 (1 H, ddd, *J* 13.2, 7.26 and 4.95, 3-H), 1.99 (1 H, ddd, *J* 12.87, 6.6 and 0.99, 2 β -H), 2.22 (1 H, ddd, *J* 12.87, 10.22 and 1.65, 2 α -H), 2.68–2.89 (2 H, m, 4-H₂), 2.94–3.07 (1 H, m, 1 α -H), 3.26 (1 H, dd, *J* 11.22 and 6.6, CH₂OH), 3.36 (1 H, dd, *J* 11.22 and 7.59, CH₂OH), 3.54 (1 H, d, *J* 10.23, 1-H), 7.04–7.08 (1 H, m, ArH) and 7.10–7.19 (3 H, m, ArH); *m/z* 204 (M⁺, 0.15), 186 [(M – H₂O)⁺, 23.4], 168 [(M – 2 H₂O)⁺, 36.4], 146 (79.2) and 128 (100%) [Found: (M – H₂O)⁺, 186.1041. C₁₃H₁₄O requires M, 186.1045].

(±)-(1 α ,2 α ,8 β α)-2 α -Hydroxy-1,2,2a,3,4,8b-hexahydrocyclobuta[a]naphthalene-1-methyl Acetate **14.**—To a solution of the cyclobutanol **12** (238 mg, 1.16 mmol) and triethylamine (0.144 cm³, 1.39 mmol) in THF (5 cm³) was added a solution of acetyl chloride (0.099 cm³, 1.39 mmol) in THF (5 cm³) dropwise at 0 °C. The solution was stirred for 3 h and then filtered to remove any precipitates. Removal of the solvent gave a residue, which was dissolved in a mixture of diethyl ether and water. The aqueous layer was extracted with diethyl ether. The combined ether phases were washed successively with water and brine, and dried over anhydrous Na₂SO₄. Evaporation of the solvent gave a residue, which was purified by PLC (1:1 ethyl acetate–hexane) to give acetate **14** (266 mg, 93%), ν_{\max} (neat)/cm⁻¹ 3402, 1738, 1246 and 743; δ_{H} (270 MHz) 1.88–2.04 (5 H, m, 2-H₂, OH and 3-H₂), 2.10 (3 H, s, OAc), 2.21–2.27 (1 H, m, 1 β -H), 2.68 (1 H, td, *J* 15.83 and 4.62, 4-H), 2.88 (1 H, ddd, *J* 15.84, 8.91 and 6.93, 4-H), 3.07 (1 H, d, *J* 7.59, 1 β -H), 4.21 (1 H, dd, *J* 11.21 and 5.94, CH₂OAc), 4.33 (1 H, dd, *J* 11.21 and 5.61, CH₂OAc) and 7.08–7.17 (4 H, m, ArH); *m/z* 246 (M⁺, 6.8), 186 [(M – MeCO₂H)⁺, 40.9] and 146 (100%) (Found: M⁺, 246.1270. C₁₅H₁₈O₃ requires M, 246.1256).

(±)-(1 α ,2 α β ,8 β β)-2 α -Hydroxy-1,2,2a,3,4,8b-hexahydrocyclobuta[a]naphthalene-1-methyl Acetate-**15.**—To a solution of the cyclobutanol **13** (28 mg, 0.14 mmol) and triethylamine (0.022 cm³, 0.16 mmol) in THF (1 cm³) was dropwise added a solution of acetyl chloride (0.011 cm³, 0.16 mmol) in THF (1 cm³) at 0 °C. The solution was stirred for 1 h at room

temperature and was then filtered. Removal of the solvent gave a residue, which was extracted with diethyl ether. The extract was worked up as described for the acetylation of the isomeric cyclobutanol **12**. The product was purified by PLC (1:1 ethyl acetate–hexane) to give *acetate 15* (34 mg, 99%) as an oil, $\nu_{\max}(\text{neat})/\text{cm}^{-1}$ 3338 (OH), 1738 (OAc), 1245 and 744; $\delta_{\text{H}}(270 \text{ MHz})$ 1.71–1.90 (2 H, m, 3-H₂), 1.91 (3 H, s, OAc), 2.01 (1 H, dd, *J* 13.2 and 6.6, 2 α -H), 2.26 (1 H, ddd, *J* 13.2, 9.9 and 1.65, 2 β -H), 2.76 (1 H, ddd, *J* 16.17, 7.29 and 4.95, 4-H), 2.83 (1 H, ddd, *J* 16.17, 7.62 and 5.28, 4-H), 3.05–3.15 (1 H, m, 1 β -H), 3.57 (1 H, d, *J* 10.23, 8 β -H), 3.69 (1 H, dd, *J* 11.22 and 7.59, CH₂OAc), 3.73 (1 H, dd, *J* 11.21 and 7.92, CH₂OAc), 6.99–7.04 (1 H, m, ArH) and 7.09–7.12 (3 H, m, ArH); *m/z* 246 (M⁺, 1.7), 186 (32.5), 168 (12.9), 157 (10.2), 146 (100), 129 (53.0), 117 (26.2), 116 (20.5), 115 (26.1), 91 (13.8) and 43 (47.4%) (Found: M⁺, 246.1263).

Photoaddition of 2-(Trimethylsiloxy)indene 16 with Acrylonitrile 2.—A solution of enol ether **16** (700 mg, 3.43 mmol), acrylonitrile **2** (3.22 g, 44.8 mmol), and Michler's ketone (150 mg, 0.56 mmol) in benzene (25 cm³) was irradiated for 16 h as described for the photoaddition of 3-trimethylsiloxy-1,2-dihydronaphthalene **1**. After evaporation of the solvent, the residue was subjected to Kugelrohr distillation to give a crude product (871 mg; 85 °C/0.15 mmHg), which was distilled into THF (5 cm³). The solution was treated with aq. HCl (5 drops) at 0 °C for 15 min and worked up as described for the photoproducts **3** and **4**. The product was subjected to PLC (1:3 ethyl acetate–hexane) to give (\pm)-(2 α ,2 α ,7 α)-7 α -hydroxy-2,2 α ,7,7 α -tetrahydro-1H-cyclobuta[a]indene-2-carbonitrile **19** (326 mg, 51%) as a more mobile oily product, $\nu_{\max}(\text{neat})/\text{cm}^{-1}$ 3400 (OH) and 2240 (CN); $\delta_{\text{H}}(270 \text{ MHz})$ 2.49 (1 H, s, OH), 2.56 (1 H, ddd, *J* 9.24, 7.26 and 4.95, 2 β -H), 2.68 (1 H, dd, *J* 12.54 and 7.26, 1 β -H), 2.76 (1 H, dd, *J* 12.54 and 9.24, 1 α -H), 3.19 (1 H, d, *J* 17.49, 7-H), 3.32 (1 H, d, *J* 17.49, 7-H), 3.94 (1 H, d, *J* 4.95, 2 α -H) and 7.25 (4 H, s, ArH); *m/z* 185 (M⁺, 9.2) and 132 [(M – CH₂=CHCH)⁺, 100%] (Found: M⁺, 185.0840. C₁₂H₁₁NO requires M, 185.0835).

The more polar product **20** was the 2 α ,2 α ,7 α ,7 α -isomer (172 mg, 27%), m.p. 108–109.5 °C (from diethyl ether–hexane), $\nu_{\max}/\text{cm}^{-1}$ 3400 (OH) and 2235 (CN); $\delta_{\text{H}}(270 \text{ MHz})$ 2.10 (1 H, s, OH), 2.50 (1 H, dd, *J* 12.82 and 8.06, 1 α -H), 2.65 (1 H, dddd, *J* 12.82, 9.53, 3.30 and 1.10, 1 β -H), 3.12 (1 H, d, *J* 16.85 and 1.10, 7 β -H), 3.26 (1 H, d, *J* 16.85, 7 α -H), 3.73 (1 H, ddd, *J* 9.53, 8.43 and 8.06, 2 β -H), 4.81 (1 H, dd, *J* 8.43 and 3.30, 2 α -H) and 7.25–7.35 (4 H, m, ArH); *m/z* 185 (M⁺, 13.3), 167 [(M – H₂O)⁺, 2.7] and 132 [(M – CH₂=CHCN)⁺, 100%] (Found: C, 77.7; H, 6.0; N, 7.6. C₁₂H₁₁NO requires C, 77.81; H, 5.99; N, 7.56%).

(\pm)-(2 α ,2 α ,7 α)-7 α -Hydroxy-2,2 α ,7,7 α -tetrahydro-1H-cyclobuta[a]indene-1-methanol **25** and its (2 α ,2 α ,7 α)-Isomer **26** by Photoaddition of 2-(Trimethylsiloxy)indene **16** with Methyl Acrylate **7**.—A solution of indene derivative **16** (2.4 g, 11.8 mmol), methyl acrylate **7** (13.0 cm³) and Michler's ketone (386 mg, 1.44 mmol) in benzene (90 cm³) was irradiated for 24 h as described for the photoaddition of dihydronaphthalene derivative **1**. After evaporation of the solvent, the residue was extracted with diethyl ether. Evaporation of the extract gave a residue, which was subjected to PLC (1:6 ethyl acetate–hexane) to give a yellow liquid (1.808 mg, 62%) which was a mixture of photoadducts **21** and **22**.

To a stirred suspension of LiAlH₄ (218 mg, 5.74 mmol) in diethyl ether (10 cm³) was added dropwise a mixture of adducts **21** and **22** in diethyl ether (10 cm³) dropwise at 0 °C while being stirred. The mixture was stirred for 1 h at 0 °C, and then aq. sodium thiosulfate was added. After the mixture had been filtered, the filtrate was dried over anhydrous Na₂SO₄.

Evaporation of the solvent gave a mixture of alcohols **23** and **24** (1.499 g), which was dissolved in THF. To the solution was then added conc. hydrochloric acid (5 drops) at 0 °C, and the solution was stirred for 30 min before being poured into water. The aqueous mixture was subsequently extracted with diethyl ether. The combined extracts were washed successively with aq. sodium hydrogen carbonate, water and brine, and dried over anhydrous Na₂SO₄. Removal of the solvent gave a thick liquid, which was subjected to PLC (1:1 ethyl acetate–hexane) to give the more mobile (*R_f* 0.17) (2 α ,2 α ,7 α)-cyclobutanol **25** (428 mg, 39% from compound **16**) and the less mobile (*R_f* 0.15) (2 α ,2 α ,7 α)-cyclobutanol **26** (316 mg, 29% from compound **16**).

The cyclobutanol **25**, m.p. 105–108 °C (from diethyl ether–hexane); $\nu_{\max}/\text{cm}^{-1}$ 3066 (OH), 1099, 1040 and 744; $\delta_{\text{H}}(270 \text{ MHz})$ 1.95 (1 H, ddd, *J* 12.87, 7.92 and 0.99, 1 α -H), 2.36 (1 H, dt, *J* 12.87, 2.64 and 0.99, 1 β -H), 2.94–3.10 (1 H, m, 2 β -H), 3.15 (2 H, d, *J* 6.6, CH₂OH), 3.23–3.39 (2 H, m, 7-H₂), 3.73 (1 H, dd, *J* 9.23 and 2.64, 2 α -H) and 7.14–7.26 (4 H, m, ArH); *m/z* 190 (M⁺, 5.3), 172 [(M – H₂O)⁺, 67.7] and 132 [(M – CH₂=CHCH₂OH)⁺, 100%] (Found: C, 75.7; H, 7.5. C₁₂H₁₄O₂ requires C, 75.76; H, 7.42%).

The cyclobutanol **26**, m.p. 113–115 °C (from dichloromethane–hexane); $\nu_{\max}/\text{cm}^{-1}$ 3066 (OH), 1099, 1039 and 744; $\delta_{\text{H}}(270 \text{ MHz})$ 2.05–2.16 (2 H, m, 1-H₂), 2.39–2.49 (1 H, m, 2 β -H), 3.18 (2 H, s, 7-H₂), 3.46 (1 H, d, *J* 2.64, 2 α -H), 3.84 (1 H, dd, *J* 10.23 and 3.96, CH₂OH), 3.94 (1 H, dd, *J* 10.23 and 3.63, CH₂OH) and 7.13–7.25 (4 H, m, ArH); *m/z* 190 (M⁺, 5.2), 172 [(M – H₂O)⁺, 67.0] and 132 [(M – CH₂=CH-CH₂OH)⁺, 100] (Found: C, 75.6; H, 7.5%).

(\pm)-(2 α ,2 α ,7 α)-7 α -Hydroxy-2,2 α ,7,7 α -tetrahydro-1H-cyclobuta[a]indene-2-methyl Acetate **27**.—To a solution of the cyclobutanol **25** (418 mg, 2.19 mmol) in THF (10 cm³) under nitrogen were added dropwise triethylamine (0.413 cm³, 3.23 mmol) and then a solution of acetyl chloride (0.21 cm³, 3.23 mmol) in THF (10 cm³) at 0 °C. The solution was stirred for 2 h and filtered so as to remove the precipitates. After evaporation of the solvent, the organic layer was washed with water. The washings were extracted with diethyl ether. The combined ether layers were washed successively with aq. sodium hydrogen carbonate, water and brine, and then dried over anhydrous Na₂SO₄. Removal of the solvent gave a product, which was subjected to PLC (1:1 ethyl acetate–hexane) to give the *acetate 27* (494 mg, 97%) as a liquid, $\nu_{\max}(\text{neat})/\text{cm}^{-1}$ 3372 (OH), 1738 (C=O), 1244 and 747; $\delta_{\text{H}}(270 \text{ MHz})$ 1.95 (1 H, ddd, *J* 12.86, 9.57 and 0.99, 1 α -H), 2.00 (3 H, s, OAc), 2.09 (1 H, s, OH), 2.39 (1 H, dddd, *J* 13.2, 9.57, 2.97 and 0.99, 1 β -H), 3.10–3.19 (3 H, m, 7-H₂ and 2 β -H), 3.70 (1 H, dd, *J* 11.22 and 8.58, CH₂OAc), 3.72 (1 H, d, *J* 8.24, 2 α -H), 3.79 (1 H, dd, *J* 11.22 and 6.6, CH₂OAc) and 7.10–7.26 (4 H, m, ArH); *m/z* 232 (M⁺, 0.39), 172 [(M – MeCO₂H)⁺, 33.2] and 129 (100%) (Found: M⁺, 232.1082. C₁₄H₁₆O₃ requires M, 232.1100).

(\pm)-(2 α ,2 α ,7 α)-7 α -Hydroxy-2,2 α ,7,7 α -tetrahydro-1H-cyclobuta[a]indene-2-methyl Acetate **28**.—To a solution of the cyclobutanol **26** (306 mg, 1.60 mmol) in THF (10 cm³) under nitrogen were added successively triethylamine (0.323 cm³, 2.31 mmol) and a solution of acetyl chloride (0.164 cm³, 2.31 mmol) in THF (10 cm³) at 0 °C. The solution was stirred for 3 h, filtered, and then worked up as described for the acetylation of the (2 α ,2 α ,7 α)-isomer **25**. The product was subjected to PLC (1:1 ethyl acetate–hexane) to give *acetate 28* as a liquid (331 mg, 89%), $\nu_{\max}(\text{neat})/\text{cm}^{-1}$ 3398 (OH), 1742 (OAc), 1240 and 748; $\delta_{\text{H}}(270 \text{ MHz})$ 2.02–2.10 (2 H, m, 2 β - and 1 α -H), 2.12 (3 H, s, OAc), 2.24 (1 H, s, OH), 2.41–2.51 (1 H, m, 1 β -H), 3.16 (1 H, d, *J* 17.49, 7-H), 3.32 (1 H, d, *J* 17.39, 7-H), 3.35 (1 H, d, *J* 4.62, 2 α -H), 4.28 (1 H, dd, *J* 10.88 and 6.6, CH₂OAc), 4.32 (1 H, dd,

J 10.88 and 5.94, CH_2OAc) and 7.12–7.25 (4 H, m, ArH); m/z 232 (M^+ , 0.62), 172 [$(\text{M} - \text{MeCO}_2\text{H})^+$, 33.3] and 129 (100%) (Found: M^+ , 232.1086. $\text{C}_{14}\text{H}_{16}\text{O}_3$ requires M , 232.1100).

Fused Cyclobutanols 32 and 33 by [2 + 2] Photoaddition of β -Suberone Trimethylsilyl Enol Ether 29 with Acrylonitrile 2.—A solution of enol ether **29** (1.815 g, 7.8 mmol), acrylonitrile **2** (6.6 cm^3) and Michler's ketone (350 g, 1.30 mmol) in benzene (45 cm^3) was irradiated under nitrogen for 18 h with Pyrex-filtered light generated from a 500 W Hg arc lamp. After the solution had been filtered, the solvent was removed by evaporation to give a yellow liquid. This was then subjected to PLC (1:5 ethyl acetate–hexane) to give *cis,cis*-adduct **30** (289 mg; R_f 0.65) and *cis,trans*-adduct **31** (210 mg; R_f 0.59). To a solution of each adduct in THF (5 cm^3) was added conc. hydrochloric acid. Each solution was stirred at room temperature for 1 h and poured into water. The solutions were extracted with diethyl ether. The extracts were worked up in the usual manner. The products were purified by PLC (1:2 ethyl acetate–hexane) to give the crystalline cyclobutanols **32** (168 mg, 10.1% from enol ether **29**) and **33** (120 mg, 7.1% from enol ether **29**).

The cyclobutanol **32**, m.p. 122–123 °C (from acetone); $\nu_{\text{max}}/\text{cm}^{-1}$ 3466 (OH), 2244, 1096, 798 and 742; $\delta_{\text{H}}^*(270 \text{ MHz})$ 1.54–1.66 (3 H, m, 3-H and 4-H₂), 1.87–1.96 (1 H, m, 3-H), 2.27 (1 H, s, OH), 2.46 (1 H, dd, *J* 12.11 and 9.57, 2 β -J), 2.53 (1 H, dd, *J* 12.21 and 8.91, 2 α -H), 2.51–2.59 (1 H, m, 5-H), 2.83 (1 H, ddd, *J* 8.58, 8.91 and 9.57, 1 β -H), 3.02 (1 H, dt, *J* 12.87 and 6.6, 5-H), 4.40 (1 H, d, *J* 8.57, 9 $\beta\alpha$ -H) and 7.09–7.17 (4 H, m, ArH); m/z 213 (M^+ , 1.2), 195 [$(\text{M} - \text{H}_2\text{O})^+$, 12.4], 156 (94.2) and 115 (100%) (Found: C, 78.9; H, 7.25; N, 6.6. $\text{C}_{14}\text{H}_{15}\text{NO}$ requires C, 78.84; H, 7.09; N, 6.57%).

The cyclobutanol **33**, m.p. 148–152 °C (from acetone); $\nu_{\text{max}}/\text{cm}^{-1}$ 3454 (OH), 2246, 1099, 799 and 742; $\delta_{\text{H}}(270 \text{ MHz})$ 1.71–1.84 (2 H, m, 4-H₂), 1.86–1.97 (1 H, m, 3-H), 2.12–2.13 (2 H, m, OH and 3-H), 2.35 (1 H, dd, *J* 12.53 and 2.79, 2 α -H), 2.57 (1 H, ddd, *J* 13.86, 6.27 and 2.31, 5-H), 2.61 (1 H, dd, *J* 12.54 and 10.23, 2 β -H), 3.07 (1 H, dt, *J* 13.86 and 5.94, 5-H), 3.58 (1 H, ddd, *J* 10.23, 10.23 and 2.96, 1 β -H), 4.04 (1 H, d, *J* 10.22, 9 $\beta\beta$ -H) and 7.01–7.29 (4 H, m, ArH); m/z 213 (M^+ , 1.3), 195 [$(\text{M} - \text{H}_2\text{O})^+$, 18.3], 156 (100) and 115 (99.7%) (Found: C, 78.7; H, 7.2; N, 6.7%).

Ring Expansion of Fused Cyclobutanol 5 via β -Scission of the Alkoxy Radical generated by Photolysis of the Corresponding Hypoiodite.—(a) *With HgO–I₂ reagent.* A stirred solution of the cyclobutanol **5** (100 mg, 0.5 mmol) in benzene (32 cm^3) containing red mercury(II) oxide (325 mg, 1.5 mmol) and iodine (381 mg, 1.5 mmol) was irradiated for 2 h, with Pyrex-filtered light generated by a 100 W high-pressure Hg arc lamp, under nitrogen. After the solution was filtered through Celite, diethyl ether was added. The solution was washed successively with 5% aq. sodium thiosulfate and water, and dried over anhydrous Na_2SO_4 . Removal of the solvent gave a product, which was subjected to PLC (1:2 ethyl acetate–hexane) to give *cis*-5-iodo-8-oxo-5,6,7,8,9,10-hexahydrobenzo[8]annulene-6-carbonitrile **34** (96 mg, 59%), m.p. 145–146 °C (from diethyl ether–hexane); $\nu_{\text{max}}/\text{cm}^{-1}$ 2242 (CN), 1707 (C=O) and 1109; $\delta_{\text{H}}(270 \text{ MHz}; \text{Et}_2\text{O})$ 2.30–2.39 (2 H, m, 7-H₂), 2.69 (1 H, dt, *J* 11.55 and 4.95, 9-H), 2.78 (1 H, td, *J* 12.54 and 4.95, 9-H), 2.92 (1 H, dt, *J* 11.54 and 3.3, 10-H), 3.02 (1 H, td, *J* 12.54 and 4.62, 10-H), 3.57 (1 H, ddd, *J* 10.89, 5.94 and 4.95, 6 β -H), 5.18 (1 H, d, *J* 4.95, 5 β -H), 7.19 (1 H, dd, *J* 7.59 and 1.65, 3-H), 7.31–7.45 (2 H, m, 1-H and

2-H) and 7.90 (1 H, d, *J* 7.59, 4-H); m/z 325 (M^+ , 4.48) and 198 [$(\text{M} - \text{I})^+$, 100%] (Found: M^+ , 324.9955. $\text{C}_{13}\text{H}_{12}\text{INO}$ requires M , 324.9965).

(b) *With (diacetoxyiodo)benzene and iodine.* A stirred solution of compound **5** (50 mg, 0.25 mmol) in benzene (16 cm^3) containing (diacetoxyiodo)benzene (163 mg, 0.51 mmol) and iodine (190 mg, 0.74 mmol) was irradiated, with Pyrex-filtered light, under nitrogen. The solution was then filtered through Celite, and the filtrate was washed successively with 5% aq. sodium thiosulfate and water. To the solution was added diethyl ether. The solution was washed successively with 5% aq. sodium carbonate and brine, and dried over anhydrous Na_2SO_4 . Removal of the solvent gave a solid residue, which was subjected to PLC (1:2 ethyl acetate–hexane) to give *trans*-5-iodo-8-oxo-5,6,7,8,9,10-hexahydrobenzo[8]annulene-6-carbonitrile **35** (33 mg, 41%), m.p. 131–132 °C (from diethyl ether–hexane); $\nu_{\text{max}}/\text{cm}^{-1}$ 2230 (CN) and 1693 (C=O); $\delta_{\text{H}}(270 \text{ MHz})$ 2.30–2.40 (2 H, m, 7-H₂), 2.60–2.70 (1 H, m, 9-H), 2.81 (1 H, dt, *J* 11.73 and 5.13, 9-H), 3.00–3.21 (2 H, m, 10-H₂), 3.23–3.50 (1 H, m, 6 β -H), 5.27 (1 H, d, *J* 10.62, 5 α -H), 7.15–7.20 (1 H, m, ArH), 7.25–7.40 (2 H, ArH) and 7.60–7.75 (1 H, m, 4-H); m/z 325 (M^+ , 6.1) and 198 [$(\text{M} - \text{I})^+$, 100%] (Found: M^+ , 324.9955).

(c) *With Pb(OAc)₄–I₂ reagent.* A stirred solution of the cyclobutanol **5** (53 mg, 0.27 mmol) in benzene (16 cm^3) containing 90% lead tetraacetate (393 mg, 0.80 mmol) and iodine (203 mg, 0.80 mmol) was irradiated for 2.5 h, with Pyrex-filtered light generated by a 100 W high-pressure Hg arc, under nitrogen. After the reaction mixture had been filtered through Celite, the filtrate was washed successively with 5% aq. sodium thiosulfate and water. To the solution was added diethyl ether; the mixture was then washed successively with 5% aq. sodium hydrogen carbonate and brine, and dried over anhydrous Na_2SO_4 . Removal of the solvent gave a residue, which was purified by PLC (1:2 ethyl acetate–hexane) to give compound **35** (47 mg, 54%).

Ring Expansion of the Fused Cyclobutanol 6 via β -Scission of the Alkoxy Radical generated by Photolysis of the Corresponding Hypoiodite.—(a) *With HgO–I₂ reagent.* A stirred solution of the cyclobutanol **6** (240 mg, 1.2 mmol) in benzene (75 cm^3) containing red HgO (782 mg, 3.6 mmol) and iodine (913 mg, 3.6 mmol) was irradiated with Pyrex-filtered light for 2 h, as in the case of the isomeric cyclobutanol **5**. The reaction mixture was worked up, as in the case of the ring-expansion reaction of the isomeric cyclobutanol **5**, to give *trans*-compound **35** (228 mg, 74%), m.p. 131–132 °C (from diethyl ether–hexane); $\nu_{\text{max}}/\text{cm}^{-1}$ 2230 (CN) and 1693 (C=O); $\delta_{\text{H}}(270 \text{ MHz})$ 2.30–2.40 (2 H, m, 7-H), 2.60–2.70 (1 H, m, 9-H), 2.81 (1 H, dt, *J* 11.73 and 5.13, 9-H), 3.00–3.21 (2 H, m, 10-H₂), 3.23–3.50 (1 H, m, 6 β -H), 5.27 (1 H, d, *J* 10.62, 5 α -H), 7.15–7.20 (1 H, m, ArH), 7.26–7.37 (2 H, m, ArH) and 7.60–7.75 (1 H, m, 4-H); m/z 325 (M^+ , 6.1) and 198 [$(\text{M} - \text{I})^+$, 100%] (Found: M^+ , 324.9955. $\text{C}_{13}\text{H}_{12}\text{INO}$ requires M , 324.9965).

(b) *With (diacetoxyiodo)benzene and iodine.* A stirred solution of the cyclobutanol **6** (49 mg, 1.25 mmol) in benzene (16 cm^3) containing (diacetoxyiodo)benzene (238 mg, 0.74 mmol) and iodine (187 mg, 0.74 mmol) was irradiated for 2 h with Pyrex-filtered light (as mentioned above). Work-up of the solution (as mentioned for the ring expansion of the cyclobutanol **5**) gave a product, which was subjected to PLC to give *trans*-substituted product **35** (43 mg, 52%).

(c) *With Pb(OAc)₄–I₂ Reagent.* A stirred solution of the cyclobutanol **6** (50 mg, 0.25 mmol) in benzene (16 cm^3) containing 90% lead tetraacetate (370 mg, 0.75 mmol) and iodine (190 mg, 0.75 mmol) was irradiated for 2.5 h with Pyrex-filtered light (as mentioned above). The solution was worked up as described for the ring expansion of cyclobutanol **5** to give a

* NMR locants follow the numbering scheme shown in Scheme 3.

product. Its purification by PLC gave *trans*-compound **35** (41 mg, 51%).

Ring Expansion of the Cyclobutanol 10 via β -Scission of the Alkoxy Radical generated by Photolysis of the Corresponding Hypoiodite.—(a) *With HgO–I₂ Reagent.* A stirred solution of the cyclobutanol **10** (50 mg, 0.215 mmol) in benzene (14 cm³) containing red HgO (219 mg, 1.01 mmol) and iodine (262 mg, 1.01 mmol) was irradiated for 1 h with Pyrex-filtered light. The solution was worked up as described for the ring expansion of cyclobutanol **5**. The product was subjected to PLC (1:2 ethyl acetate–hexane) to give (\pm)-methyl (1 α ,11 α ,12 α)-10-oxotricyclo[9.1.0.0^{2,7}]dodeca-2,4,6-triene-12-carboxylate **36** (16 mg, 32%) as the more mobile product (*R_f* 0.45) and (\pm)-methyl (2 α ,3 α)-tetrahydro-2-[2-(2-iodoethyl)phenyl]-5-oxotetrahydrofuran-3-carboxylate **39** (12 mg, 15%) (*R_f* 0.33).

Compound 36: m.p. 101–103 °C (from diethyl ether–hexane); $\nu_{\max}/\text{cm}^{-1}$ 3034 (cyclopropane CH), 1728 (CO₂Me) and 1708 (C=O); δ_{H} (270 MHz) 2.28 (1 H, dd, *J* 4.62 and 4.95, 12 β -H), 2.56 (1 H, ddd, *J* 16.50, 11.55 and 4.28, 9-H), 2.77 (1 H, dd, *J* 10.56 and 4.95, 11 α -H), 2.77–2.83 (1 H, m, 9-H), 2.87–2.97 (1 H, m, 8-H), 2.96 (1 H, dd, *J* 10.56 and 4.61, 1 α -H), 3.48 (1 H, ddd, *J* 11.55, 13.86 and 4.94, 8-H), 3.77 (3 H, s, OMe), 7.08–7.23 (3 H, m, ArH), and 7.33–7.36 (1 H, m, ArH); *m/z* 230 (M⁺, 4.5), 198 [(M – MeOH)⁺, 91.9] and 129 (100%) (Found: C, 72.7; H, 6.0. C₁₄H₁₄O₃ requires C, 73.03; H, 6.13%).

Compound 39: m.p. 73–74 °C; $\nu_{\max}/\text{cm}^{-1}$ 1768 (lactone C=O), 1734 (C=O), 1204, 1011 and 762; δ_{H} (270 MHz) 2.89 (1 H, dd, *J* 17.58 and 8.79, 4 β -H), 3.10 (1 H, dd, *J* 17.58 and 2.93, 4 α -H), 3.19 (3 H, s, OMe), 3.15–3.45 (4 H, m, CH₂CH₂I), 3.70 (1 H, ddd, *J* 8.79, 7.32 and 2.93, 3 β -H), 5.95 (1 H, d, *J* 7.33, 2 β -H) and 7.15–7.35 (4 H, m, ArH); *m/z* 374 (M⁺, 0.02), 247 [(M – I)⁺, 20.5] and 133 (100%) (Found: C, 44.85; H, 4.04; I, 33.7. C₁₄H₁₅O₄I requires C, 44.93; H, 4.04; I, 33.92%).

(b) *With (diacetoxyiodo)benzene and iodine.* A stirred solution of the cyclobutanol **10** (50 mg, 0.215 mol) in benzene (14 cm³) containing (diacetoxyiodo)benzene (326 mg, 1.01 mmol) and iodine (262 mg, 1.01 mmol) was irradiated for 1 h with Pyrex-filtered light (as described above). Work-up of the solution and separation of its products (as described for the photolysis of the hypoiodite of the cyclobutanol **5**) gave (\pm)-methyl (1 α ,11 α ,12 α)-10-oxotricyclo[9.1.0.0^{2,7}]dodeca-2,4,6-triene-12-carboxylate **36**, (*R_f* 0.31; 7 mg, 14%), methyl 8-oxo-7,8,9,10-tetrahydrobenzo[8]annulene-6-carboxylate **37** (*R_f* 0.23; 11 mg, 22%), and methyl *trans*-5-acetoxy-8-oxo-5,6,7,8,9,10-hexahydro[8]annulene-6-carboxylate **38** (*R_f* 0.2; 33 mg, 53%) in order of their mobility on TLC (1:3 ethyl acetate–hexane).

Compound 37: $\nu_{\max}/\text{cm}^{-1}$ 1711 and 1636 (C=O and α,β -unsaturated ester) and 757; δ_{H} (270 MHz) 2.63–2.67 (2 H, m, 9-H), 2.93–2.98 (2 H, m, 10-H₂), 3.35 (2 H, s, 7-H₂), 3.86 (3 H, s, OMe), 7.19–7.23 (1 H, m, ArH), 7.25–7.35 (3 H, m, ArH) and 7.90 (1 H, s, 5-H); *m/z* 230 (M⁺, 3.88), and 198 [(M – MeOH)⁺, 100%] (Found: M⁺, 230.0955. C₁₄H₁₄O₃ requires M, 230.0943).

Compound 38: m.p. 112–114 °C (from diethyl ether–hexane); $\nu_{\max}/\text{cm}^{-1}$ 1734 (OAc and CO₂Me) and 1707 (C=O); δ_{H} (270 MHz) 2.07 (3 H, s, OAc), 2.20 (1 H, dd, *J* 12.2 and 4.62, 7 β -H), 2.52 (1 H, dt, *J* 12.21 and 4.62, 9-H), 2.70 (1 H, dd, *J* 12.21 and 6.6, 7 α -H), 2.80 (1 H, td, *J* 12.2 and 3.96, 9-H), 2.89 (1 H, ddd, *J* 10.56, 4.62 and 6.6, 6 β -H), 2.99 (1 H, td, *J* 13.86 and 4.62, 10-H), 3.28 (1 H, dt, *J* 13.86 and 3.3, 10-H), 3.79 (3 H, s, OMe), 6.17 (1 H, d, *J* 10.55, 5 α -H), 7.19–7.22 (1 H, m, ArH) and 7.23–7.25 (3 H, m, ArH). Irradiation of the signal at δ 2.20 decoupled the signal at δ 2.89 to a doublet, and irradiation of the signal at δ 6.17 also decoupled the signal at δ 2.89 to a doublet; *m/z* 290 (M⁺, 1.81), 230 [(M – HOAc)⁺, 13.05] and 43 (100%) (Found: C, 66.0; H, 6.3. C₁₆H₁₈O₅ requires C, 66.20; H, 6.25%).

(c) *With Pb(OAc)₄ and iodine.* A stirred solution of the cyclobutanol **10** (50 mg, 0.215 mmol) in benzene (14 cm³) containing 90% Pb(OAc)₄ (498 mg, 1.01 mmol) and iodine (262 mg, 1.01 mmol) was irradiated with Pyrex-filtered light for 1 h. The solution was worked up as mentioned above. The product was subjected to PLC (1:2 ethyl acetate–hexane) to give the benzo[8]annulene **37** (*R_f* 0.5; 6 mg, 12%) and its acetic acid adduct **38** (*R_f* 0.29; 48 mg, 77%).

Ring Expansion of the Cyclobutanol 11 via β -Scission of the Alkoxy Radical generated by Photolysis of the Corresponding Hypoiodite.—(a) *With HgO–I₂ Reagent.* A stirred solution of the cyclobutanol **11** (50 mg, 0.215 mmol) in benzene (14 cm³) containing red HgO (219 mg, 1.01 mmol) and iodine (262 mg, 1.01 mmol) was irradiated with Pyrex-filtered light for 1 h 15 min (as mentioned above). Work-up of the solution, followed by separation of its products by PLC (1:2 ethyl acetate–hexane), gave compound **37** (*R_f* 0.57; 12 mg, 34%) and **36** (*R_f* 0.44; 17 mg, 24%).

(b) *With (diacetoxyiodo)benzene and iodine.* A stirred solution of the cyclobutanol **11** (50 mg, 0.215 mmol) in benzene (14 cm³) containing (diacetoxyiodo)benzene (326 mg, 1.01 mmol) and iodine (262 mg, 1.01 mmol) was photolysed with Pyrex-filtered light for 1 h 15 min. The solution was worked up as described above to give a product mixture. Separation of the products by PLC (1:2 ethyl acetate–hexane) gave compound **37** (*R_f* 0.60; 8 mg, 28%), compound **36** (*R_f* 0.49; 7 mg, 14%), and compound **38** (*R_f* 0.29; 11 mg, 18%).

(c) *With Pb(OAc)₄–I₂.* A stirred solution of the cyclobutanol **11** (50 mg, 0.215 mmol) in benzene (14 cm³) containing 90% Pb(OAc)₄ (498 mg, 1.01 mmol) and iodine (262 mg, 1.01 mmol) was irradiated for 1 h 10 min. The solution was worked up as described above. The products were separated by PLC (1:2 ethyl acetate–hexane) to give compound **37** (*R_f* 0.60; 5 mg, 11%) and compound **38** (*R_f* 0.31; 21 mg, 34%).

Ring Expansion of the Cyclobutanol 14 via β -Scission of the Alkoxy Radical generated by Photolysis of the Corresponding Hypoiodite in the Presence of HgO–I₂ Reagent.—A stirred solution of the cyclobutanol **14** (50 mg, 0.20 mmol) in benzene (14 cm³) containing red HgO (205 mg, 0.95 mmol) and iodine (245 mg, 0.95 mmol) was irradiated under nitrogen for 1 h with Pyrex-filtered light generated from a 100 W Hg arc lamp. The reaction mixture was worked up as described above. The product was subjected to PLC (1:2 ethyl acetate–hexane) to give 9-acetoxy-methyl-10-iodo-5,6,7,8,9,10-hexahydrobenzo[8]-annulene-7-one **40** (*R_f* 0.38; 12 mg, 16%) and 4-acetoxymethyl-5-[2-(2-iodoethyl)phenyl]tetrahydrofuran-2-one **41** (*R_f* 0.24; 24 mg, 31%).

Compound 40: $\nu_{\max}/\text{cm}^{-1}$ 1741, 1707, 1231 and 734; δ_{H} (270 MHz) 2.01 (3 H, s, AcO), 2.01–2.23 (2 H, m, 8-H₂), 2.3–2.5 (1 H, m, 9-H), 2.59 (1 H, ddd, *J* 12.46, 9.53 and 3.67, 6-H), 2.74 (1 H, ddd, *J* 12.46, 8.80 and 4.03, 6-H), 2.93 (1 H, ddd, *J* 14.29, 8.80 and 3.69, 5-H), 3.48 (1 H, ddd, *J* 14.29, 9.53 and 4.03, 5-H), 3.91 (1 H, dd, *J* 10.99 and 8.43, CH₂OAc), 4.41 (1 H, dd, *J* 10.99 and 5.06, CH₂OAc), 5.46 (1 H, d, *J* 3.30, 10-H) and 7.05–7.3 (4 H, m, ArH); *m/z* 245 [(M – I)⁺, 2.0], 185 [(M – MeCO₂H)⁺, 72.1] and 43 (100%) [Found: C₁₅H₁₇O₃, 245.1177. (M – I) requires *m/z*, 245.1178].

Compound 41: $\nu_{\max}/\text{cm}^{-1}$ 2924, 1772, 1736, 1265 and 744; δ_{H} (270 MHz) 1.92 (3 H, s, AcO), 2.64 (1 H, d, *J* 17.48 and 2.59, 3 α -H), 2.96 (1 H, dd, *J* 17.48 and 8.58, 3 β -H), 3.11–3.23 (3 H, m, CH₂CH₂I and 4-H), 3.32–3.38 (2 H, m, CH₂CH₂I), 3.56 (1 H, dd, *J* 11.55 and 6.60, CH₂OAc), 3.78 (1 H, dd, *J* 11.72 and 5.50, CH₂OAc), 5.88 (1 H, d, *J* 6.59, 5-H), 7.21–7.26 (1 H, m, ArH), 7.28–7.34 (2 H, m, ArH) and 7.43–7.46 (1 H, m, ArH); *m/z* 388 (M⁺, 0.35), 328 [(M – MeCO₂H)⁺, 2.79] and 43 (100%)

(Found: C, 46.4; H, 4.4; I, 32.8. $C_{15}H_{17}IO_4$ requires C, 46.41; H, 4.41; I, 32.69%).

Ring Expansion of the Cyclobutanol 15 via β -Scission of the Alkoxy Radical generated by Photolysis of the Corresponding Hypoiodite in the Presence of $HgO-I_2$ Reagent.—A stirred solution of the cyclobutanol **15** (25 mg, 0.10 mmol) in benzene (7 cm³) containing red HgO (103 mg, 0.48 mmol) and iodine (121 mg, 0.48 mmol) was irradiated for 1 h in the same manner as in the case of the cyclobutanol **14**. The reaction mixture was worked up as mentioned above. The product was subjected to PLC (1:2 ethyl acetate–hexane) to give compound **40** (13 mg, 24%) and the furanone **41** (24 mg, 31%).

Ring Expansion of Fused Cyclobutanol 19 via β -Scission of the Alkoxy Radical generated by Photolysis of the Corresponding Hypoiodite. (With $HgO-I_2$ Reagent).—A solution of the cyclobutanol **19** (178 mg, 0.96 mmol) in benzene (50 cm³) containing red HgO (600 mg, 2.88 mmol) and iodine (740 mg, 2.88 mmol) was irradiated for 2.5 h as described above. The solution was worked up as described above, and the products were purified by PLC (1:3 ethyl acetate–hexane) to give 8-oxo-8,9-dihydro-7H-benzo[7]annulene-6-carbonitrile **42** (27 mg, 20%), m.p. 91–93 °C (from diethyl ether–hexane); $\nu_{max}(neat)/cm^{-1}$ 2215 (CN), 1715 (C=O) and 1618; δ_H (270 MHz) 3.26 (2 H, s, 7-H₂), 3.71 (2 H, s, 9-H₂), 7.39 (4 H, br s, ArH) and 7.67 (1 H, s, 5-H); m/z 183 (M^+ , 71), 155 [($M - CO$)⁺, 93.1] and 115 (100%) (Found: C, 78.9; H, 4.9; N, 7.65. $C_{12}H_9NO$ requires C, 78.67; H, 4.95; N, 7.65%).

Ring Expansion of Fused Cyclobutanol 20 via β -Scission of the Alkoxy Radical generated by Photolysis of the Corresponding Hypoiodite. (With $HgO-I_2$ Reagent).—A solution of the cyclobutanol **20** (204 mg, 1.10 mmol) in benzene (60 cm³) containing red HgO (724 mg, 3.3 mmol) and I₂ (848 mg, 3.3 mmol) was irradiated for 2 h as described above for the cyclobutanol **19**. Work-up of the solution and separation of the product (as described above) gave product **42** (56 mg, 28%).

Photolysis of the Hypoiodite of the Cyclobutanol 27, prepared in situ by Reaction with Mercury(II) Oxide and Iodine Reagent in Benzene.—A stirred solution of the cyclobutanol **27** (50 mg, 0.215 mmol) in benzene (15 cm³) containing red HgO (140 mg, 0.645 mmol) and iodine (164 mg, 0.645 mmol) was irradiated as described for the photolysis in the previous experiment. After the reaction mixture had been worked up by the usual method, the product was subjected to PLC to give 4-acetoxymethyl-5-[2-(iodomethyl)phenyl]tetrahydrofuran-2-one **44** (R_f 0.36; 6 mg, 7%) and 1-[2-acetoxy-1-(iodomethyl)ethyl]-3,4-dihydro-1H-2-benzopyran-3-one **43** (R_f 0.30; 12 mg, 15%).

Compound 43; ν_{max}/cm^{-1} 1746 (AcO), 1230 (CH₂I) and 751; δ_H (270 MHz) 2.04 (3 H, s, OAc), 2.42–5.5 (1 H, m, 1'-H), 3.25–3.4 (2 H, m, 4-H₂), 3.7–3.85 (2 H, m, CH₂I), 4.0–4.45 (2 H, m, 2'-H₂), 5.46 and 5.66 (combined 1 H, 2 d, J 5.49 and 6.6, 1-H) and 7.2–7.4 (4 H, m, ArH); m/z 374 (M^+ , 1.6), 332 ($M - CH_2=C=O$, 2.2) and 119 (100%) (Found: M^+ , 374.0060. $C_{14}H_{15}IO_4$ requires M , 374.0016).

Compound 44; ν_{max}/cm^{-1} 1784 (lactone C=O), 1738 (AcO), 1235 and 762; δ_H (270 MHz) 2.12 (3 H, s, OAc), 2.51 (1 H, dd, J 17.59 and 5.86, 3-H), 2.84 (1 H, dd, J 17.59 and 8.43, 3-H), 2.9–3.05 (1 H, m, 4-H), 4.49 (1 H, dd, J 11.36 and 7.20, CH₂OAc), 4.52 (2 H, s, CH₂I), 4.59 (1 H, dd, J 11.36 and 5.50, CH₂OAc), 5.72 (1 H, d, J 5.13, 5-H) and 7.25–7.45 (4 H, m, ArH); m/z 374 (M^+ , 1.1), 332 ($M - CH_2=C=O$, 2.4) and 119 (100%) (Found: M^+ , 374.0008. $C_{14}H_{15}IO_4$ requires M , 374.0016).

Photolysis of the Hypoiodite of the Cyclobutanol 28 prepared in situ by Reaction with Mercury(II) Oxide and Iodine Reagent in Benzene.—A stirred solution of the cyclobutanol **28** (50 mg,

0.215 mmol) in benzene (15 cm³) containing red HgO (140 mg, 0.645 mmol) and iodine (164 mg, 0.645 mmol) was irradiated for 1.5 h under the conditions described for the cyclobutanol **27**. The product was subjected to PLC to give 4-acetoxymethyl-5-[2-(iodomethyl)phenyl]tetrahydrofuran-2-one **44** (R_f 0.36; 5 mg, 6%) and 1-[2-acetoxy-1-(iodomethyl)ethyl]-3,4-dihydro-1H-2-benzopyran-3-one **43** (R_f 0.30; 10 mg, 12%).

Ring Expansion of Fused Cyclobutanol 32 via β -Scission of the Alkoxy Radical generated by Photolysis of the Corresponding Hypoiodite. (With $HgO-I_2$ Reagent).—A stirred solution of the cyclobutanol **32** (50 mg, 0.23 mmol) in benzene (16 cm³) containing red HgO (152 mg, 0.70 mmol) and iodine (178 mg, 0.70 mmol) was irradiated for 2 h 50 min as in the photolysis of the hypoiodite of the cyclobutanol **28**. The solution was worked up as usual. The residue was subjected to PLC (1:2 ethyl acetate–hexane) to give (±)-(5 β ,6 α)-5-iodo-8-oxo-6,7,8,9,10,11-hexahydro-5H-benzo[9]annulene-6-carbonitrile **45** (R_f 0.29; 66 mg, 85%) and its (5 α ,6 α)-isomer **46** (R_f 0.40; 9 mg, 12%).

Compound 45; m.p. 159–161 °C (from acetone); $\nu_{max}(neat)/cm^{-1}$ 2240, 1704 and 746; δ_H 1.95–2.06 (2 H, m, 10-H₂) 2.27–2.36 (1 H, m, 9-H), 2.43 (1 H, dd, J 15.18 and 5.94, 7 α -H), 2.50 (1 H, dd, J 15.18 and 2.97, 7 β -H), 2.64–2.73 (1 H, m, 9-H), 2.77–2.86 (1 H, m, 11-H), 2.94–2.99 (1 H, m, 11-H), 3.63 (1 H, ddd, J 11.55, 5.94 and 2.97, 6 β -H), 5.61 (1 H, d, J 11.55, 5 α -H), 7.06–7.13 (1 H, m, ArH), 7.25–7.32 (2 H, m, ArH) and 7.61–7.64 (1 H, m, ArH); m/z 212 [($M - I^+$), 44.77%] (Found: C, 49.15; H, 4.1; N, 4.2; I, 37.3. $C_{14}H_{14}INO$ requires C, 49.58; H, 4.16; N, 4.13; I, 37.42%).

Compound 46; $\nu_{max}(neat)/cm^{-1}$ 2242, 1706 and 747; δ_H 1.61–1.66 (1 H, m, 10-H), 1.87–1.96 (1 H, m, 10-H), 2.16–2.29 (2 H, m, 9-H₂), 2.34–2.46 (1 H, m, 7 α -H), 2.49–2.84 (3 H, m, 7 β -H and 11-H₂), 3.95 (1 H, ddd, J 11.88, 5.61 and 5.28, 6 β -H), 5.47 (1 H, d, J 5.61, 5 β -H), 7.09–7.14 (1 H, m, ArH), 7.19–7.38 (2 H, m, ArH) and 8.01–8.05 (1 H, m, ArH); m/z 212 [($M - I^+$), 34.42] and 115 (100%) [Found: ($M - I^+$), 212.1096. $C_{14}H_{14}NO$ requires m/z , 212.1075].

Ring Expansion of Fused Cyclobutanol 33 via β -Scission of the Alkoxy Radical generated by Photolysis of the Corresponding Hypoiodite (With $HgO-I_2$ Reagent).—A stirred solution of the cyclobutanol **33** (33 mg, 0.16 mmol) in benzene (11 cm³) containing red HgO (101 mg, 0.46 mmol) and iodine (118 mg, 0.46 mmol) was irradiated for 2.5 h. Work-up of the solution as in the case of the photolysis of the hypoiodite of isomer **32** gave products **45** and **46** in 46 and 11% yield, respectively.

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