Photo-induced Molecular Transformations. Part 87.[1] Ring Expansion through [2 + 2] Photocycloaddition-β-Scission Sequences; Synthesis of Benzohomotropones from 1- and 2-Naphthols and Methyl Acrylate

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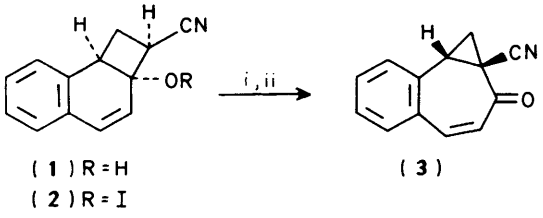
Photolysis of 4-substituted tricyclo[6.4.0.0^{2,5}]dodeca-1(12),6,8,10-tetraen-5-ols (**9**), (**10**), and (**12**), derived in three-steps from the regioselective photocycloadducts formed from 2-naphthyl trimethylsilyl ether and methyl acrylate, in the presence of HgO–I_2 in benzene, to give the benzocyclo-octenone derivatives (**11**), (**13**), and (**14**) which arise from β-scission of their fused bond. The benzocyclo-octenones cyclized with base in DMF to give benzohomotropones, 4-substituted tricyclo-[6.4.0.0^{2,4}]dodeca-1(12),6,8,10-tetraen-2-ones (**15**) and (**16**). Similar photolyses of 3-substituted tricyclo[6.4.0.0^{2,5}]dodeca-1(12),6,8,10-tetraen-2-ols (**24**) and (**25**), prepared in three steps from the regioselective [2 + 2] photocycloadduct (**19**) formed from 1-naphthyl trimethylsilyl ether with methyl acrylate, in the presence of HgO–I_2 in benzene, gives the benzocyclo-octenone (**26**) in rather low yield. Treatment of the latter with a base in DMF gave a benzohomotropone, 3-substituted tricyclo-[6.4.0.0^{3,5}]dodeca-1(12),6,8,10-tetraen-2-one (**27**).

In our previous paper[2] we reported that the irradiation of the hypoiodite (**2**) of *endo*-4-cyanotricyclo[6.4.0.0^{2,5}]dodeca-1(12),6,8,10-tetraen-5-ol (**1**),[3] derived from the [2 + 2] photocycloaddition of 2-naphthol with acrylonitrile, in benzene led to the formation of 4-cyanotricyclo[6.4.0.0^{2,4}]dodeca-1(12),6,8,10-tetraen-5-one (**3**); the latter arose from a β-scission of the cyclobutanoxyl radical (Scheme 1).

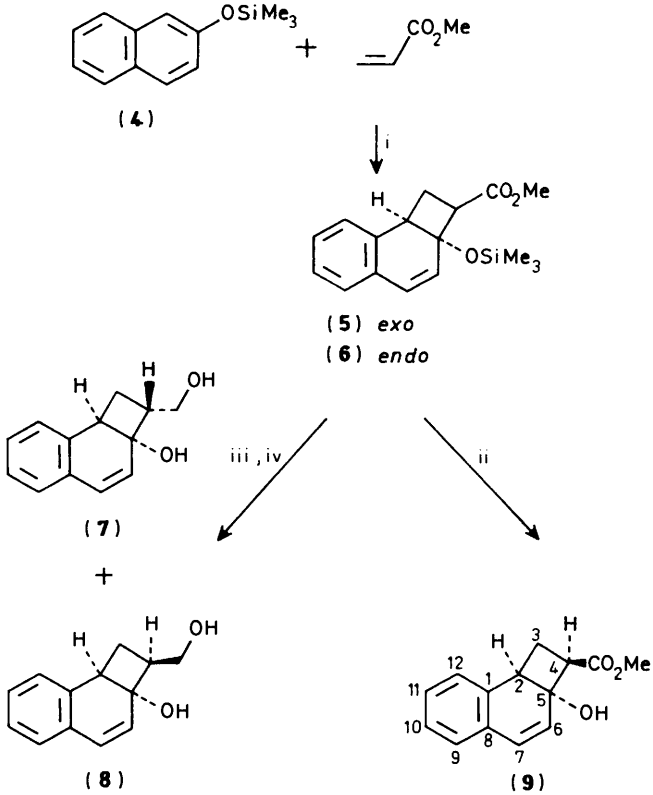


Scheme 1. *Reagents and conditions:* i, HgO–I_2–C_6H_6; ii, *hν*

In this paper we report an extension of this synthetically useful process that consists of first a [2 + 2] photocycloaddition of the trimethylsilyl ether of 1- or 2-naphthol with methyl acrylate, second removal of the trimethylsilyl group from the resulting cyclobutanols, and third β-scission of the alkoxyl radical generated by the irradiation of the hypoiodite of the latter.

Results

Ring Expansion via β-*Scission of the Cyclobutanoxyl Radicals derived from the Photocycloadducts formed from 2-Naphthyl Trimethylsilyl Ether and Methyl Acrylate.*—We found that in contrast to the [2 + 2] photocycloaddition of 2-naphthol with acrylonitrile,[2,3] none of the photocycloadducts was obtained on irradiation with a Pyrex-filtered light of 2-naphthol with an excess of methyl acylate in t-butyl alcohol–isopropyl alcohol. We found, however, that a mixture of *exo* and *endo* adducts (**5**) and (**6**) could be obtained in a 57% yield when 2-naphthyl trimethylsilyl ether and an excess of methyl acrylate in t-butyl alcohol–isopropyl alcohol were irradiated with a Pyrex-filtered light.



Scheme 2. *Reagents and conditions:* i, Bu^{t}OH–Pr^{i}OH (1:1), *hν*; ii, aqueous MeOH–HCl, 0 °C; iii, $LiAlH_4$–EtOEt, 0 °C; iv, aqueous THF–aqueous HCl, 0 °C

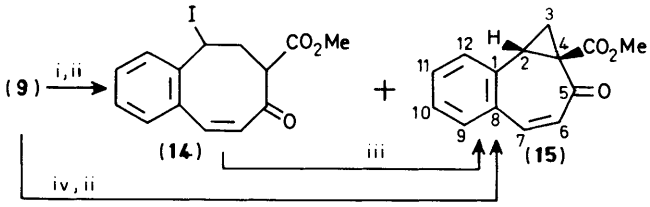
Acidic hydrolysis of the oily mixture of the *endo* and *exo* cycloadducts in methanol with a few drops of concentrated hydrochloric acid at 0 °C for 10 min gave only a crystalline cyclobutanol (**9**); this was the major product (48% from naphthyl trimethylsilyl ether) of this photocycloaddition. The ^{1}H n.m.r. spectrum of cyclobutanol (**9**) showed overlapping

signals at δ 3.55 and 3.54 as a triplet of a doublet (*J* 10.63 and 1.47 Hz) and a doublet of a doublet (*J* 10.63 and 1.47 Hz) assignable to 2-H and the 4-H. It also showed a quartet centred at δ 1.80 (*J* 10.63 Hz) and a multiplet at δ 2.15—2.31 assignable to the 3-methylene protons. The coupling constants of these protons were very similar to those of the *endo*-photocycloadduct of 2-methoxynaphthalene with acrylonitrile prepared by Chamberlain and McCullough.[4] The *trans* orientation of the hydroxy and the methoxycarbonyl group of cyclobutanol (**9**) was then confirmed by transforming it to the diol (**8**) and by comparing its ^{1}H n.m.r. spectrum with that of the *exo* isomer (**7**) (*vide infra*). The more strained *exo* isomer (**5**), which should be more susceptible to the acid-catalysed retroaldol reaction, was not isolated in this acidic hydrolysis.

Reduction of the mixture of the cycloadducts (**5**) and (**6**) with lithium aluminium hydride in diethyl ether at 0 °C, followed by hydrolysis of the resulting alcohols with hydrochloric acid gave a mixture of the *exo*- and *endo*-cyclobutanols (**7**) and (**8**). This mixture was separable by means of preparative t.l.c. with silica gel to give the crystalline *exo*- (**7**) and *endo*-diols (**8**) in 45 and 14% yields. The *endo*-diol (**8**) was identical with the diol obtained by the reduction of the cyclobutanol (**9**) with lithium aluminium hydride. The *exo* and *endo* stereochemistry of the diols (**7**) and (**8**) was clearly distinguished by a comparison of their ^{1}H n.m.r. spectra. Thus, the ^{1}H n.m.r. spectrum of the *exo* diol (**7**) exhibited its 2-H as a broad triplet at δ 3.77 (*J* 9.53 and 10.26), one of the 3-methylene protons as a multiplet at δ 1.57 (ddd, *J* 11.36, 9.53, and 8.80), another proton of the C-3 methylene group as a multiplet at δ 1.90 (ddd, *J* 11.36, 10.26, and 2.57 Hz), the 4-H as a multiplet at δ 2.6—2.65, and the hydroxymethylene protons as two separated multiplets at δ 4.1—4.2 and 3.85—3.9. In contrast, the ^{1}H n.m.r. spectrum of the *endo* diol (**8**) exhibited the 2-H as a doublet of a doublet at δ 3.50 (*J* 9.16 and 9.89), the C-3 methylene protons as a doublet of a triplet at δ 1.13 (*J* 10.63 and 9.89) and a doublet of a triplet at δ 2.18 (*J* 10.63 and 9.16), the 4-H as a multiplet at δ 2.85—3.0, and the hydroxymethylene protons as a doublet at δ 3.76 (*J* 7.32). Comparisons of the above spectral results for the *endo* and *exo* isomers indicated that the signals due to 2-H, one of the 3-Hs, and the methylene protons carrying the hydroxy group of the *exo* isomer (**7**) appeared at lower fields than those due to the corresponding proton of the *endo* isomer (**8**). These downfield shifts are explained by the deshielding by the hydroxymethylene and 5-hydroxy group. Moreover, the signal due to the 4-H of the *endo* isomer (**8**) appeared at lower field than the 4-H of the *endo* isomer (**7**). This downfield shift is also explained by deshielding by the 5-hydroxy group of the *endo* isomer (**8**). The assigned stereochemistry is in agreement with the pattern of the splitting of the signals due to the hydroxymethylene groups of the *endo* and *exo* isomers: while the two protons of the hydroxymethylene group of isomer (**8**) are equivalent, those of the geometrically more constrained hydroxymethylene group of isomer (**7**) are not and show hindered rotation.

Photolysis of the *endo* cyclobutanol (**9**) in benzene containing mercury(II) oxide, iodine, and a few drops of pyridine in a Pyrex vessel with a 100-W high-pressure Hg arc for 2 h under nitrogen gave a crystalline product (**15**) in 51% yield. The molecular formula was established as $C_{14}H_{12}O_3$ by means of mass spectrometry and elemental analysis. The structure of the product was deduced as methyl 5-oxotricyclo[6.4.0.0^{2,4}]-dodeca-1(12),6,8,10-tetraene-4-carboxylate on the basis of the spectroscopic evidence (Scheme 3) (see Experimental section).

We found that when this photolysis is conducted without the addition of pyridine the product before purification with preparative t.l.c. is not the benzohomotropone (**15**). We found, however, that it can be transformed into the latter if it is subjected either to preparative t.l.c. on silica gel plates or treated with pyridine. From this we deduced that the product obtained through photolysis in the absence of pyridine is the benzocyclo-octenone (**14**).

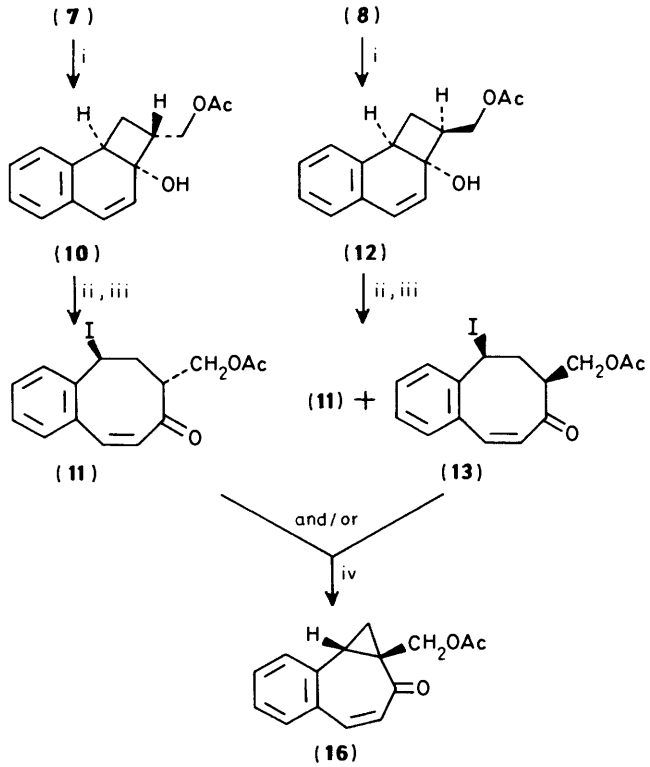


Scheme 3. *Reagents and conditions:* i, HgO–I_2–C_6H_6; ii, *hν*; iii, pyridine or SiO_2; iv, HgO–I_2–pyridine

Treatment of the mixture of cyclobutanyl trimethylsilyl ethers (**5**) and (**6**) in DMF with a solution of $FeCl_3$ in DMF [5] failed to give any product derived from the ring expansion and resulted only in the formation of the parent cyclobutanols.

Selective acetylation of the diols (**7**) and (**8**) with acetyl chloride and triethylamine in diethyl ether at 0 °C gave the corresponding liquid monoacetates (**10**) and (**12**).

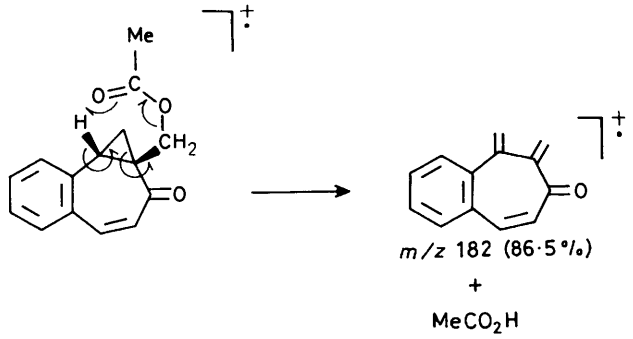
Irradiation of the cyclobutanol (**10**) in benzene containing mercury(II) oxide and iodine as in the case of the cyclobutanol (**9**) but without the addition of pyridine gave a single liquid product (**11**) containing iodine in a 47% yield. High resolution mass spectrometry established the molecular formula to be $C_{15}H_{15}IO_3$. The i.r. spectrum revealed two strong bands at 1 733 and 1 654 cm^{-1}; these were assignable to an acetoxy and an α,β-unsaturated carbonyl group. These spectral results together with the analysis of the ^{1}H n.m.r. spectrum (see Experimental section) clearly indicated that the product (**11**) is a benzocyclo-octenone (Scheme 4). Although we have no evidence about the relative configuration of the iodine and the



Scheme 4. *Reagents and conditions:* i, AcCl–Et_3N–EtOEt, 0 °C; ii, HgO–I_2–C_6H_6; iii, hv; iv, THF–NaH

acetoxymethylene substituents, the two substituents are most likely *trans* oriented since the bulky iodine molecule may combine with a benzocyclo-octenyl radical (generated by the β-scission) from the face opposite that where the acetoxymethylene group is located. Similar photolysis of the isomeric cyclobutanol (**12**) gave a mixture of products. Analysis of the i.r., mass, and ^{1}H n.m.r. spectra (see Experimental section) showed that the products are a mixture of *trans* (**11**) and *cis* isomers (**13**). Formation of the mixture of the diastereoisomers from the *endo*-cyclobutanol (**12**) contrasts with the results of the *exo*-cyclobutanol (**10**). The abstraction in this case of an iodine atom from an iodine molecule by a cyclo-octenyl radical is probably made mainly from the face opposite to the acetoxymethyl substituent to give the iodide (**11**) while a portion of the iodine atom generated from the hypoiodite may approach from the same face as the acetoxymethyl substituent to give the iodide (**13**).

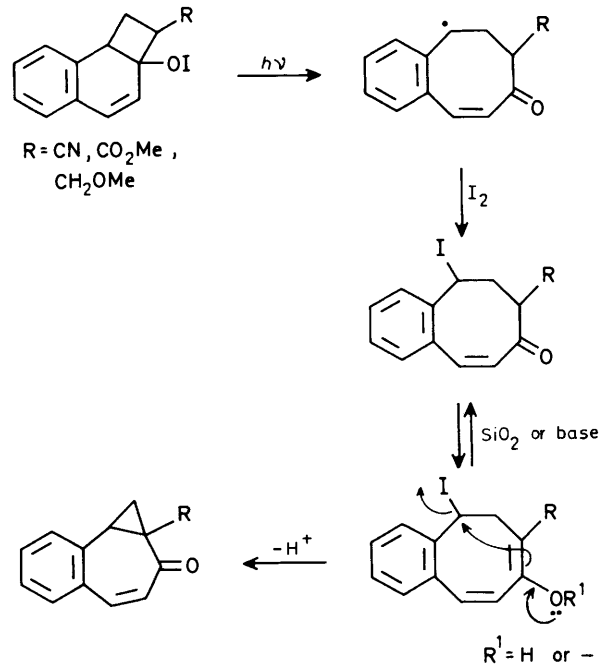
Treatment of the benzocyclo-octenone (**11**) in THF with sodium hydride at room temperature for 18 h gave a crystalline product (**16**) in a 60% yield. Analysis of the various spectra of the product (see Experimental section) indicated that it is a benzohomotropone (**16**) (see Scheme 4). The electron impact mass spectrum (e.i. m.s.) of the benzohomotropone (**16**) exhibited an intense fragment ion of *m/z* 182 (86.5%). The structure and the genesis of the ion are outlined in Scheme 5.



Scheme 5.

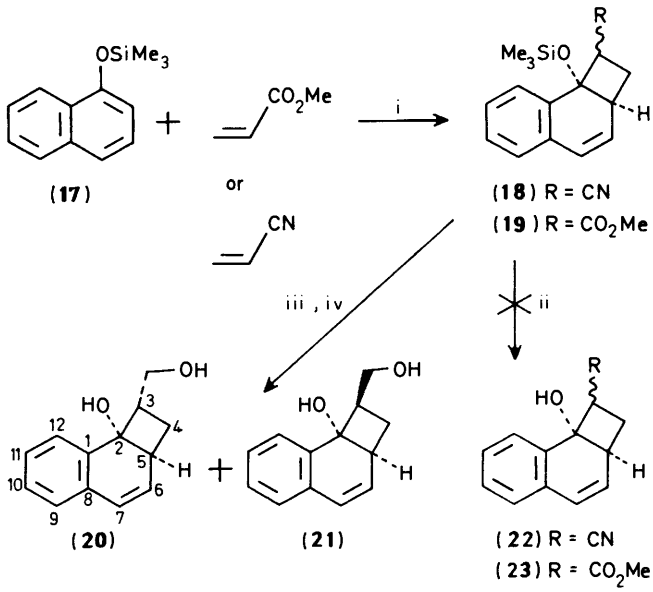
The foregoing result proved that the benzohomotropones including benzohomotropone (**3**) previously reported by us [2] is formed through cyclization of the initial benzocyclo-octenone derivatives such as (**11**), as suggested in our previous paper.[2] Formation of benzohomotropones by photolysis of *exo*- and *endo*-4-substituted tricyclo[6.4.0.0^{2,5}]dodeca-1(12),6,8,10-tetraen-5-yl hypoiodite is thought to proceed by the path shown in Scheme 6. It is evident that formation of the cyclopropane ring by cyclization of the benzocyclo-octenones carrying the cyano or methoxycarbonyl group occurs so readily that intramolecular displacement of the iodine takes place even in the absence of added base.

Ring Expansion via β-*Scission of Cyclobutanoxyl Radicals derived from the Photocycloadducts between α-Naphthyl Trimethylsilyl Ether and Acrylonitrile or Methyl Acrylate.*—We then extended our ring expansion to a ring expansion of the photoadduct of 1-naphthol with acrylonitrile [3] and methyl acrylate. Akhtar and McCullough [3] have already reported that photoaddition of 1-naphthyl trimethylsilyl ether (**17**) with acrylonitrile gives the trimethylsilyl ether of 3-cyanotricyclo-[6.4.0.0^{2,5}]dodeca-1(12),6,8,10-tetraen-2-ol (**18**) in a low yield. We found that the acid-catalysed removal of the trimethylsilyl group from the adduct (**18**) led mostly to formation of a 1-naphthol derivative by means of a retro-aldol reaction and cyclobutanol (**22**) was obtained in only very poor yield.



Scheme 6.

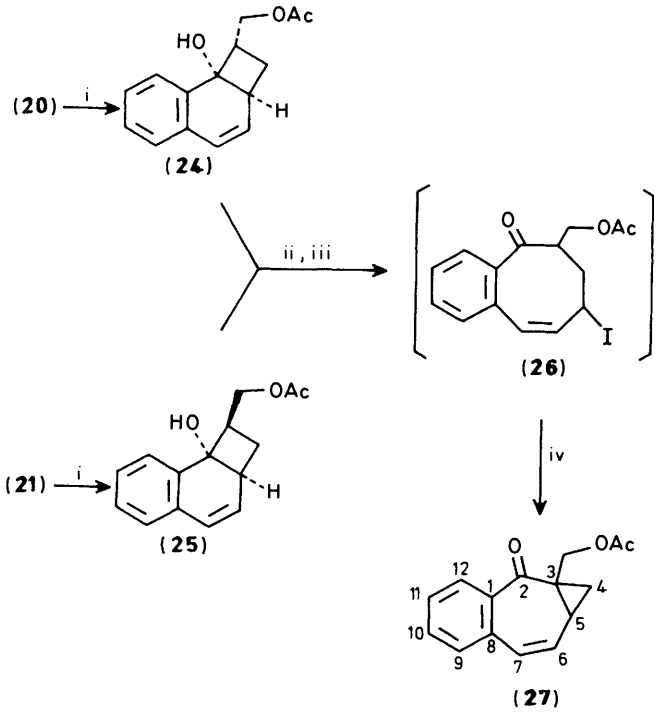
Photoaddition of compound (**17**) with methyl acrylate in t-butyl alcohol–isopropyl alcohol (1:1) took place in a regioselective manner and gave a mixture of *exo* and *endo* adducts (**19**) (Scheme 7). Acid-catalysed removal of the protecting group of the adduct (**19**) again failed to give the cyclobutanols (**23**) and led to 1-naphthol derivatives by a retro-aldol reaction. The adduct (**19**) was, therefore, subjected to reduction with lithium aluminium hydride at 0 °C and to acid-catalysed hydrolysis to give the *exo*- (**20**) and *endo*-diol (**21**). These isomers were separable by preparative t.l.c. The isolated



Scheme 7. *Reagents and conditions:* i, Bu^{t}OH–Pr^{i}OH (1:1); ii, aqueous MeOH–HCl; iii, $LiAlH_4$–EtOEt, 0 °C; iv, aqueous THF–aqueous HCl, 0 °C

yields of the *exo* diol (**20**) and the *endo*-diol (**21**) from 1-naphthyl trimethyl ether were 19 and 13%, respectively.

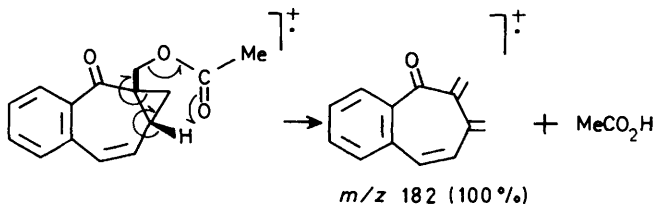
Selective acetylation of the diols (**20**) and (**21**) with acetyl chloride in diethyl ether containing triethylamine at 0 °C gave the corresponding monoacetates (**24**) and (**25**) (Scheme 8).



Scheme 8. *Reagents and conditions:* i, AcCl–Et_3N–EtOEt, 0 °C; ii, HgO–I_2–C_6H_6; iii, *hν*; iv, NaH–DMF

The *exo* and *endo* stereochemistry of these cyclobutanols could clearly be distinguished by ^1H n.m.r. spectroscopy. Thus, comparisons of *exo*- and *endo*-cyclobutanols revealed that the signals for the methylene protons of the acetoxymethylene group of the *exo* isomer (**24**) shifted downfield (δ 4.21, dd, *J* 11.72 and 5.86 Hz and δ 4.59 dd, *J* 11.72 and 8.30 Hz) from the corresponding signal of the *endo* isomer (**25**) (a multiplet at δ 3.9—4.0). The downfield shift is attributable to deshielding by the 5-hydroxy group. The ^1H n.m.r. spectra also indicated that whilst the two methylene protons of the acetoxymethylene protons of isomer (**24**) are not equivalent those of the isomer (**25**) are nearly so. The greater hindrance of the rotation of the acetoxymethylene group of isomer (**24**) shown by the n.m.r. spectra is in accord with the assigned *exo* geometry which should be geometrically more constrained.

Photolysis of the *exo* cyclobutanol in benzene containing mercury(II) oxide and iodine under the conditions mentioned above gave a rather complex mixture of the products including a benzocyclo-octene (**26**). The products were dissolved in DMF and treated with sodium hydride at room temperature for 0.5 h. Purification of the product by means of preparative t.l.c. gave a pure product (**27**) in 12% yield. The product was confirmed to be 3-acetoxymethyltricyclo[6.4.0.0^{3,5}]dodeca-1(12),6,8,10-tetraen-2-one (**27**) by means of i.r., mass, and ^1H n.m.r. spectroscopy (see Scheme 8 and Experimental section). Similar treatment of the *endo* diol (**25**) gave a low yield of the benzohomotropone (**27**), identical with the product obtained from the *exo* diol (**24**). As with the benzohomotropone (**16**) the e.i.m.s. of the benzohomotropone (**27**) exhibited a fragment ion



Scheme 9.

of *m/z* 182 as the base peak. Its probable structure and genesis are outlined in Scheme 9.

The foregoing experiments confirmed that the β-scission of the alkoxyl radicals generated from either 4-substituted tricyclo[6.4.0.0^{2,5}]dodeca-1(12),6,8,10-tetraen-5-ol and 3-substituted tricyclo[6.4.0.0^{2,5}]dodeca-1(12),6,8,10-tetraen-2-ol takes place at their fused bonds to give benzocyclo-octenones which can be readily cyclized to benzohomotropones with added bases although the yields of the benzocyclo-octenones from the latter are low.

Experimental

M.p.s were recorded with a Yanagimoto micro m.p. apparatus. Unless stated otherwise, i.r. spectra were determined for Nujol mulls with a Hitachi Model 285 infrared spectrometer. Unless stated otherwise, ^1H n.m.r. spectra were determined with a JEOL JNM-FX 270 NMR spectrometer operating at 270 MHz (solvent $CDCl_3$:$SiMe_4$ as internal standard) at the Faculty of Pharmaceutical Sciences. Some of the n.m.r. spectra were determined with a JEOL PS 200 high resolution FT-NMR spectrometer operating at 200 MHz (Faculty of Pharmaceutical Sciences) and a Hitachi R90B FT n.m.r. spectrometer operating at 90 MHz. T.l.c. was carried out on a Merck Kieselgel 60 PF_{254}. The high and low resolution mass spectra were determined with a JEOL JMS-D300 spectrometer (70 eV) (Faculty of Pharmaceutical Sciences). Photocycloadditions were carried out by irradiating the solution in a Pyrex vessel with a light generated by 500-W EIKOSHA PIH-500S high pressure Hg arc lamp. The lamp and the solution in the vessel were cooled by water during irradiation. The photolysis of the hypoiodites was carried out by irradiating the stirred solution in a Pyrex vessel with a light generated by a 100-W EIKOSHA PIH-100 high pressure Hg arc lamp.

1- *and* 2-*Naphthyl Trimethylsilyl Ethers.*—These silyl ethers were prepared according to the procedures reported by McCullough.[3]

Methyl endo-5-*Hydroxytricyclo*[6.4.0.0^{2,5}]*dodeca*-1(12),6,8,10-*tetraene*-4-*carboxylate* (**9**).—A mixture of 2-naphthyl trimethylsilyl ether (**4**) (2.0 g, 9.3 mmol), methyl acetylate (32 g, 370 mmol), and t-butyl alcohol–isopropyl alcohol (1 : 1; 400 ml) was irradiated with a 400-W high-pressure mercury arc through a Pyrex filter under an atmosphere of nitrogen for 24 h. The solution was then filtered through a Celite layer, the filtrate evaporated, and the residue subjected to preparative t.l.c. with ethyl acetate–hexane (1 : 3) to give the crude cycloadduct as a yellow oil (2.0 g). The adduct in methanol (5 ml) was then hydrolysed by the addition of 5 drops of concentrated hydrochloric acid at 0 °C and stirring for 10 min. The solution was extracted with diethyl ether and the extract worked up to provide the product which was recrystallized from diethyl ether to give the pure *endo* cyclobutanol (**9**) (1.02 g, 48% from 2-naphthol TMS ether), m.p. 116—118 °C (Found: M^+, 230.0925. $C_{14}H_{14}O_3$ requires *M*,

230.0943); $\nu_{max.}$ 3 430 (OH) and 1 690 cm^{-1} (CO_2Me); δ_H 1.80 (1 H, q, *J* 10.63, 3-H), 2.15—2.31 (1 H, m, 3-H), 3.54 (1 H, dd, *J* 10.63 and 8.80, 4-H), 3.55 (1 H, dt, *J* 10.63 and 1.47, 2-H), 3.75 (3 H, s, OMe), 5.73 (1 H, dd, *J* 9.90 and 1.47 Hz, 6-H), 6.68 (1 H, d, *J* 9.90, 7-H), and 7.05—7.2 (4 H, m, ArH); *m/z* 230 (M^+, 0.7%), 198 (2), 144 [$(M - CH_2{=}CHCO_2Me)^+$, 100], 115 (19.9), and 55 (23.6).

Reduction of the Photocycloadduct (**9**) *to the Diol* (**8**) *with Lithium Aluminium Hydride.*—A solution of the adduct (**9**) (705 mg, 3.06 mmol) in diethyl ether (5 ml) was added dropwise to lithium aluminium hydride (150 mg) in diethyl ether (10 ml) at 0 °C and the solution was stirred for 1.5 h. Several drops of aqueous saturated sodium sulphate were added to the solution in order to remove any excess of the reagent after which it was dried ($MgSO_4$), filtered through Celite, and evaporated under reduced pressure to give an oily residue; this was purified by preparative t.l.c. (ethyl acetate; R_H 0.50) to give the diol (**8**) (555 mg, 90%). A specimen for analysis was obtained by recrystallizing it from diethyl ether–hexane; it had m.p. 101—102 °C (Found: C, 77.15; H, 7.1. $C_{13}H_{14}O_2$ requires C, 77.20; H, 6.98%); $\nu_{max.}$ 3 270 cm^{-1} (OH); δ_H 1.13 (1 H, dt, *J* 10.63 and 9.89, 3-H), 2.18 (1 H, dt, *J* 10.63 and 9.16, 3-H), 2.85—3.0 (1 H, m, 4-H), 3.50 (1 H, dd, *J* 9.16 and 9.89, 2-H), 3.76 (2 H, d, *J* 7.32, CH_2OH), 5.90 (1 H, dd, *J* 9.89 and 1.47, 6-H), 6.72 (1 H, d, *J* 9.89, 7-H), and 7.05—7.2 (4 H, m, aromatic H); *m/z* 184 [$(M - H_2O)^+$, 1.5%], 144 [$(M - CH_2{=}CHCH_2OH)^+$, 100], and 115 (20.8).

Reduction and Hydrolysis of a Mixture of the endo *and* exo *Photocycloadducts* (**5**) *and* (**6**).—A solution of the mixture of the adducts (1.0 g, 3.3 mmol) in diethyl ether (3 ml) was added with stirring to lithium aluminium hydride (127 mg) in diethyl ether (5 ml) at 0 °C. After 0.5 h several drops of aqueous saturated sodium sulphate were added to the solution which was then stirred for an additional 10 min. It was then dried ($MgSO_4$), filtered through Celite, and evaporated to give a product which was dissolved in THF (3 ml) containing 5 drops of concentrated hydrochloric acid. The solution was stirred for 3 h, extracted with diethyl ether, and the extract washed with aqueous sodium hydrogen carbonate and water, dried, and evaporated to give an oily product. This was subjected to preparative t.l.c. with ethyl acetate to give the less polar *exo* diol (**7**) (R_F 0.7) [121 mg, 14% from (**4**)] and the more polar *endo* diol (**8**) (R_F 0.5) [411 mg, 45% from (**4**)]. Each isomer was recrystallized from diethyl ether–hexane to provide an analytical sample: *exo*-diol (**7**), m.p. 99—100 °C (Found: C, 77.05; H, 7.05. $C_{13}H_{14}O_2$ requires C, 77.20; H, 6.98%); $\nu_{max.}$ 3 300 cm^{-1} (OH); δ_H 1.57 (1 H, ddd, *J* 11.36, 9.53, and 8.80, 3-H), 1.90 (1 H, ddd, *J* 11.36, 10.26, and 2.57, 3-H), 2.6—2.65 (1 H, m, 4-H), 3.77 (1 H, br t, *J* 9.53 and 10.26, 2-H), 3.85—3.9 (1 H, m, CH_2OH), 4.1—4.2 (1 H, m, CH_2OH), 5.85 (1 H, dd, *J* 9.89 and 1.46, 6-H), 6.60 (1 H, d, *J* 9.89, 7-H), and 7.05—7.2 (4 H, m, ArH); *m/z* 184 [$(M - H_2O)^+$, 4.4%], 144 [$(M - CH_2{=}CHCH_2OH)^+$, 100], and 115 (21.5).

The *endo* diol (**8**) was identical with the diol (**8**) obtained by reduction of the *endo* adduct (**9**).

The Monoacetate (**10**) *of the* exo-*Diol* (**7**).—Acetyl chloride (46 mg, 0.59 mmol) was added to a stirred solution of the *exo* diol (**7**) (100 mg, 0.49 mmol) and triethylamine (60 mg, 0.59 mmol) in diethyl ether (3 ml) at 0 °C. The solution was stirred for 5 h and then poured into water. The aqueous layer was extracted with diethyl ether and the extract washed with aqueous sodium hydrogen carbonate and water, dried ($MgSO_4$), and evaporated to give the product. This was purified by means of preparative t.l.c. with ethyl acetate–hexane (1:1) to give the monoacetate (**10**) (R_F 0.58, 95 mg, 76%); $\nu_{max.}$(neat) 3 430 (OH) and 1 730 cm^{-1} (OAc); δ_H (200 MHz) 1.62 (1 H, m, 3-H), 2.01 (1 H, m, 3-H), 2.65—2.75 (1 H, m, 4-H), 3.70 (1 H, t, *J* 9.77 Hz, 2-H), 4.37 (1 H, dd, *J* 11.72 and 6.83 Hz, CH_2OAc), 4.57 (1 H, dd, *J* 11.72 and 7.32 Hz, CH_2OAc), 5.82 (1 H, dd, *J* 9.76 and 1.46 Hz, 6-H), 6.00 (1 H, d, *J* 9.76 Hz, 7-H), and 7.0—7.3 (4 H, m, ArH); *m/z* 244 (M^+, 0.2) and 144 [$(M - CH_2{=}CHCH_2OAc)^+$, 100] (Found: M^+, 244.1081. $C_{15}H_{16}O_3$ requires *M*, 244.1100).

The Monoacetate (**12**) *of the* endo-*Diol* (**8**).—This acetate was prepared by the same procedure as that described in the preceding experiment. The product was a liquid, R_F 0.28 (ethyl acetate–hexane, 1:3); $\nu_{max.}$(neat) 3 400 (OH) and 1 730 cm^{-1} (OAc); δ_H 1.16 (1 H, m, 3-H), 2.20 (1 H, m, 3-H), 2.07 (3 H, s, OAc), 2.9—3.05 (1 H, m, 4-H), 3.50 (1 H, dt, *J* 9.90 and 1.47 Hz, 2-H), 4.12 (1 H, dd, *J* 11.35 and 8.42 Hz, CH_2OAc), 4.19 (1 H, dd, *J* 11.35 and 6.60 Hz, CH_2OAc), 5.81 (1 H, dd, *J* 9.89 and 1.47 Hz, 6-H), 6.70 (1 H, d, *J* 9.89 Hz, 7-H), and 7.05—7.2 (4 H, m, ArH); *m/z* 244 (M^+, 0.4) and 144 [$(M - CH_2{=}CHCH_2OAc)^+$, 100] (Found: M^+, 244.1094. $C_{15}H_{16}O_3$ requires *M*, 244.1100).

Photolysis of the Cyclobutanol (**9**) *in the Presence of Mercury*(II) *Oxide and Iodine in Benzene.*—(a) *In the presence of pyridine.* The cyclobutanol (**9**) (100 mg, 0.43 mmol) in benzene (20 ml) containing mercury(II) oxide (278 mg, 1.29 mmol), iodine (327 mg, 1.29 mmol), and pyridine (1 ml) in a Pyrex vessel was irradiated for 2 h under a nitrogen atmosphere. The solution was filtered through Celite, washed with 5% aqueous $Na_2S_2O_3$, dried ($MgSO_4$), and evaporated to give a liquid which was purified by means of preparative t.l.c. to afford the benzohomotropone (**15**) (50 mg, 51%). Its recrystallization from diethyl ether–hexane gave an analytical specimen, m.p. 94 °C; R_F 0.23 (ethyl acetate–hexane, 1:5); $\nu_{max.}$ 1 739 (CO_2Me) and 1 638 cm^{-1} (α,β-unsaturated carbonyl); $\lambda_{max.}$(EtOH) 293 (ε 6 600), 231sh, and 208 nm (ε 18 300); δ_H (90 MHz) 2.06 (1 H, dd, *J* 8.35 and 5.06 Hz, 3-H), 2.33 (1 H, dd, *J* 9.67 and 5.06 Hz, 3-H), 2.92 (1 H, dd, *J* 9.67 and 8.35 Hz, 2-H), 3.81 (3 H, s, OMe), 6.03 (1 H, d, *J* 12.97 Hz, 6-H), 6.84 (1 H, d, *J* 12.97 Hz, 7-H), and 7.2—7.5 (4 H, m, ArH); *m/z* 228 (M^+, 36.7), 196 (81.0), 168 (93.4), and 141 (100) (Found: C, 73.25; H, 5.35. $C_{14}H_{12}O_3$ requires C, 73.67; H, 5.30%).

(b) *In the absence of pyridine.* In the absence of pyridine photolysis gave rise to an unstable product which was transformed partly or wholly into the benzohomotropone (**15**) during separation by preparative t.l.c. with silica gel.

Photolysis of the Cyclobutanol (**20**) *in the Presence of Mercury*(II) *Oxide and Iodine.*—This photolysis was carried by the same procedure as that described in the preceding experiment. The crude product was purified by means of preparative t.l.c. with ethyl acetate–hexane (1:3) to give a single product (**11**) as a gummy material (R_F 0.47); $\nu_{max.}$(neat) 1 733 (OAc) and 1 654 cm^{-1} (α,β-unsaturated carbonyl); δ_H (200 MHz) 1.93 (3 H, s, OAc), 2.45—2.8 (3 H, m, CH_2CHCO), 3.97 (1 H, dd, *J* 10.74 and 4.88 Hz, CH_2OAc), 4.31 (1 H, dd, *J* 10.74 and 7.81 Hz, CH_2OAc), 5.53 (1 H, dd, *J* 11.23 and 8.30 Hz, *CH*I), 6.28 (1 H, d, *J* 12.70 Hz, C=*CH*C=O), 7.20 (1 H, d, *J* 12.70 Hz, *CH*=CH–C=O), 7.20—7.5 (3 H, m, ArH), and 7.92 (1 H, d, *J* 7.82 Hz, ArH) (Found: M^+, 370.0040. $C_{15}H_{15}IO_3$ requires *M*, 370.0065).

Photolysis of the Cyclobutanol (**12**) *in the Presence of Mercury*(II) *Oxide and Iodine.*—This photolysis was carried out in a similar way to that described for the cyclobutanol (**10**). The crude product was purified by means of preparative t.l.c. as in the case of the photolysis product from the cyclobutyl hypodiodite (**10**) to give a mixture of the diastereoisomers (**11**) and (**13**); $\nu_{max.}$(neat) 1 733 (OAc) and 1 652 cm^{-1} (α,β-unsaturated carbonyl); δ_H (90 MHz) 1.93 and 1.97 (each 3 H, each s, OAc), 2.4—2.8 (3 H, m, CH_2CH), 3.85—4.55 (2 H, m, CH_2OAc), 5.4—5.75 (1 H, m, CHI), 6.28 [1 H, d, *J* 12.7 Hz, CH=*CH*CO of (**11**)], 6.40 [1 H, d, *J* 13.2 Hz, CH=*CH*CO of

(**12**)], 6.8—7.5 (4 H, m, ArH and vinylic H), and 7.8—7.95 (1 H, m, ArH).

Preparation of 4-*Acetoxymethyltricyclo*[6.4.0.0^{2,4}]*dodeca*-1(12),6,8,10-*tetraen*-5-*one* (**16**).—Sodium hydride (50% suspension in mineral oil; 10 mg, 0.2 mmol) was added at room temperature to a stirred solution of *compound* (**11**) (64 mg, 0.17 mmol) in THF (3 ml). The solution was stirred for 18 h and then quenched by adding aqueous NH_4Cl. It was then extracted with diethyl ether and the organic layer washed with water, dried ($MgSO_4$), and evaporated to give a residue which, subjected to preparative t.l.c. with ethyl acetate–hexane (1:1), yielded the benzohomotropone (**16**) (25 mg, 60%); R_F 0.59. Recrystallization of the product from diethyl ether–hexane provided an analytical specimen, m.p. 111—112.5 °C; $\nu_{max.}$(Nujol) 1 738 (OMe) and 1 636 cm^{-1} (α,β-unsaturated carbonyl); $\lambda_{max.}$(EtOH) 291 (ε 5 100), 231sh, and 208 nm (17 200); δ_H (90 MHz) 1.85 (1 H, dd, *J* 9.67 and 5.06 Hz, 3-H), 1.87 (1 H, dd, *J* 7.69 and 5.06 Hz, 3-H), 2.06 (3 H, s, OAc), 2.76 (1 H, dd, *J* 9.67 and 7.69 Hz, 2-H), 4.37 (2 H, ABq, *J* 11.65 Hz, C*H*$_2$OAc), 6.06 (1 H, d, *J* 12.97 Hz, 6-H), 6.89 (1 H, d, *J* 12.97 Hz), and 7.25—7.85 (4 H, m, ArH); *m*/*z* 242 (*M*$^+$, 12.2), 182 (86.5), and 43 (100) (Found: *M*$^+$, 242.0932. $C_{15}H_{14}O_3$ requires *M*, 252.0932).

exo- *and* endo-3-*Hydroxymethyltricyclo*[6.4.0.0^{2,5}]*dodeca*-1(12),6,8,10-*tetraen*-2-*ols* (**20**) *and* (**21**).—1-Naphthyl trimethylsilyl ether (**17**) (2.0 g, 9.3 mmol) and methyl acrylate (32 g, 370 mmol) dissolved in a butyl alcohol–isopropyl alcohol (1:1) (400 ml) were irradiated with a 400-W high-pressure mercury arc through a Pyrex filter under nitrogen for 18 h. The solution was then filtered through Celite, evaporated under reduced pressure, and the residue dissolved in diethyl ether to remove insoluble oily product. Evaporation of the solvent from the ethereal solution gave a mixture of isomeric adducts (**19**). The mixture in diethyl ether (3 ml) was added dropwise to diethyl ether (5 ml) containing lithium aluminium hydride (254 mg) at 0 °C and the solution was stirred for 0.5 h. Several drops of aqueous saturated sodium sulphate were added to the solution which was then dried ($MgSO_4$), filtered through Celite, and evaporated under reduced pressure to give an oily residue. This was dissolved in THF (3 ml) containing a few drops of concentrated hydrochloric acid and the solution stirred for 3 h. Diethyl ether was added to this solution which was then washed with aqueous sodium hydrogen carbonate and water, dried ($MgSO_4$), and evaporated under reduced pressure to give a product which was subjected to preparative t.l.c. with hexane–ethyl acetate (3:1) to provide two fractions. The more mobile fraction (358 mg, 19%) was the *exo*-diol (**20**) which was recrystallized from a hexane–diethyl ether (1:1); it had m.p. 100—101 °C (Found: C, 77.3; H, 7.0. $C_{13}H_{14}O_2$ requires C, 77.20; H, 6.98%); $\nu_{max.}$ 3 350 and 3 550 cm^{-1} (OH); δ_H (200 MHz) 1.66 (1 H, ddd, *J* 11.72, 11.23, and 8.79 Hz, 4-H), 2.05 (1 H, ddd, *J* 11.23, 10.26, and 10.25 Hz, 4-H), 2.75—2.95 (1 H, m, 3-H), 3.15—3.3 (1 H, m, 5-H), 3.8—4.1 (2 H, m, C*H*$_2$OH), 5.98 (1 H, dd, *J* 9.77 and 5.86 Hz, 6-H), 6.41 (1 H, d, *J* 9.77 Hz, 7-H), 7.05—7.1 (1 H, m, ArH), 7.2—7.35 (2 H, m, ArH), and 7.45—7.55 (1 H, m, ArH); *m*/*z* 184 [(*M* − H_2O)$^+$, 2.6%] and 144 [(*M* − CH_2=$CHCH_2OH$)$^+$, 100].

The less mobile fraction (249 mg, 13%) was an oily *endo*-diol (**21**) which could not be induced to crystallize (Found: *M*$^+$, 202.0993. $C_{13}H_{14}O_2$ requires *M*, 202.0994); $\nu_{max.}$(neat) 3 350 cm^{-1} (OH); δ_H (200 MHz) 1.14 (1 H, dt, *J* 10.74 and 9.76 Hz, 4-H), 2.27 (1 H, dt, 10.74 and 9.28 Hz, 4-H), 2.9—3.15 (2 H, m, 3- and 5-H), 3.5—3.7 (2 H, m, C*H*$_2$OH), 5.99 (1 H, dd, *J* 9.77 and 5.86 Hz, 6-H), 6.35 (1 H, d, *J* 9.77 Hz, 7-H), 7.05—7.15 (1 H, m, ArH), 7.2—7.3 (2 H, m, ArH), and 7.5—7.6 (1 H, m, ArH); *m*/*z* 202 (*M*$^+$, 0.1%), and 144 [(*M* − CH_2=$CHCH_2OH$)$^+$, 100].

exo-3-*Acetoxymethyltricyclo*[6.4.0.0^{2,5}]*dodeca*-1(12),6,8,10-*tetraen*-2-*ol* (**24**).—Acetyl chloride (55 mg, 0.71 mmol) was added to a stirred solution of the *exo* diol (**20**) (120 mg, 0.59 mmol) in diethyl ether (3 ml) at 0 °C. The solution was stirred for 5 h and then poured into water. The aqueous layer was worked up as in the acetylation of the *exo* diol (**7**). The crude product was purified by t.l.c. with a hexane–ethyl acetate (5:1) to yield the monoacetate (**24**) (128 mg) which was recrystallized from diethyl ether–hexane (1:1); it had m.p. 95—99 °C (Found: *M*$^+$, 244.1076. $C_{15}H_{16}O_3$ requires *M*, 244.1100); $\nu_{max.}$ 3 400 (OH) and 1 730 cm^{-1} (OAc); δ_H (200 MHz) 1.76 (1 H, ddd, *J* 11.23, 8.79, and 6.35 Hz, 4-H), 2.14 (1 H, ddd, *J* 11.23, 9.76, and 6.34 Hz, 4-H), 2.06 (3 H, s, OAc), 2.85—3.15 (2 H, m, 3- and 5-H), 4.21 (1 H, dd, *J* 11.72 and 5.86 Hz, C*H*$_2$OAc), 4.59 (1 H, dd, *J* 11.72 and 8.30 Hz, C*H*$_2$OAc), 5.95 (1 H, dd, *J* 9.76 and 4.88 Hz, 6-H), 6.41 (1 H, dd, *J* 9.76 Hz, 5-H), 7.0—7.1 (1 H, m, ArH), and 7.15—7.4 (3 H, m, ArH); *m*/*z* 244 (*M*$^+$, 0.4%) and 144 [(*M* − CH_2=$CHCH_2OAc$)$^+$, 100].

endo-3-*Acetoxymethyltricyclo*[6.4.0.0^{2,5}]*dodeca*-1(12),6,8,10-*tetraen*-2-*ol* (**25**).—This monoacetate was prepared from the diol (**21**) as described for the *exo*-diol (**20**). All attempts to crystallize the acetate failed; $\nu_{max.}$(neat) 3 400 (OH) and 1 734 cm^{-1} (OAc); δ_H 1.14 (1 H, q, *J* 9.89 Hz, 4-H), 1.98 (3 H, s, OAc), 2.25 (1 H, m, 4-H), 3.0—3.15 (2 H, m, 3- and 5-H), 5.98 (1 H, dd, *J* 9.90 and 5.87 Hz, 6-H), 6.36 (1 H, d, *J* 9.90 Hz, 7-H), 7.05—7.1 (1 H, m, ArH), 7.2—7.3 (2 H, m, ArH), and 7.4—7.45 (1 H, m, ArH); *m*/*z* 244 (*M*$^+$, 0.2%) and 144 [(*M* − CH_2=$CHCH_2$-OAc)$^+$, 100].

3-*Acetoxymethoxytricyclo*[6.4.0.0^{3,5}]*dodeca*-1(12),6,8,10-*tetraen*-2-one (**27**) *through Irradiation of the Hypoiodite of the Cyclobutanol* (**24**).—The cyclobutanol (**24**) (120 mg, 0.52 mmol), dissolved in benzene (30 ml) containing mercury(II) oxide (335 mg, 1.56 mmol) and iodine (393 mg, 1.56 mmol) in a Pyrex vessel, was irradiated. Work-up of the reaction mixture gave an oily product which was dissolved in DMF (2 ml). Sodium hydride (50% suspension in mineral oil; 0.52 mmol, 25 mg) was added to this solution which was stirred for 30 min and then quenched with aqueous ammonium chloride. Extraction of the solution with diethyl ether and work-up of the organic layer gave an oily product which was subjected to preparative t.l.c. with ethyl acetate–hexane (1:3) to yield the benzohomotropone (**27**) (15 mg, 12%); R_F 0.35; $\nu_{max.}$(neat) 1 734 (OAc) and 1 650 (conjugated carbonyl); δ_H 1.75 (1 H, d, *J* 8.06 Hz, 4-H), 2.05 (1 H, dd, *J* 8.06 and 7.33 Hz, 4-H), 2.09 (3 H, s, OAc), 2.20 (1 H, dd, *J* 7.33 and 6.96 Hz, 5-H), 4.24 and 4.48 (each 1 H, each d, *J* 11.72 Hz, C*H*$_2$OAc), 6.26 (1 H, dd, *J* 10.62 and 6.96 Hz, 6-H), 6.35 (1 H, d, *J* 10.62 Hz, 7-H), 7.15—7.45 (3 H, m, ArH), and 7.63 (1 H, dd, *J* 7.70 and 1.46 Hz, 12-H); *m*/*z* 242 (*M*$^+$, 25.4%) and 182 (100).

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