Photochemistry of Carbonyl-bridged Dibenzocyclodecadienes[1]

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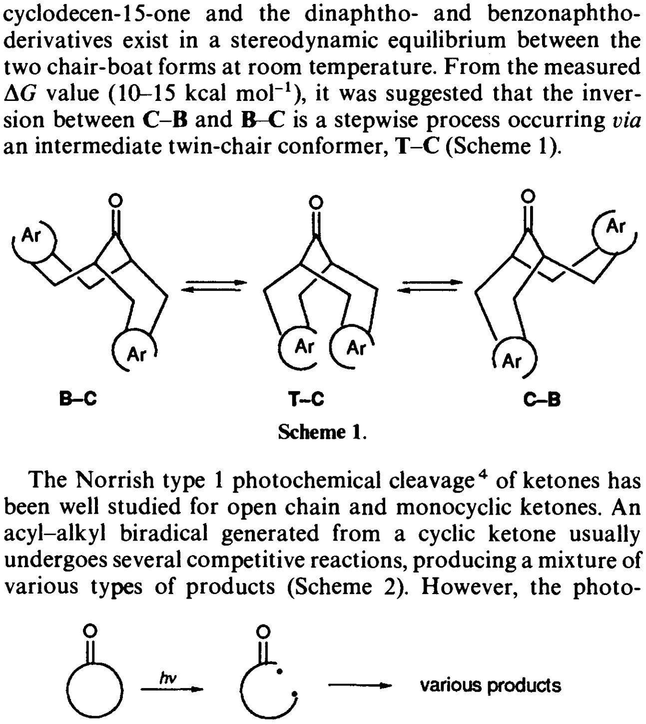
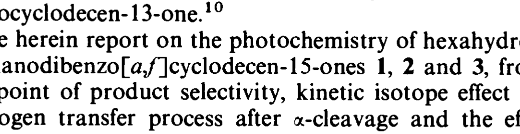
The photolyses of 5,6,7,12,13,14-hexahydro-6,13-methanodibenzo[A,F]cyclodecen-15-ones **1**, **2** and **3** have been investigated. After Norrish type 1 cleavage, diester **1** gave the alkenes *E*-**5** and *Z*-**5** *via* loss of carbon monoxide and hydrogen transfer, while **2** and **3** gave ketenes **10a** and **10b**, respectively, by transannular migration of an α-hydrogen, which was quenched with MeOH, giving the monoester **6** and diesters *cis*-**11** and *trans*-**11**, respectively. Photolysis of deuteriated **2** and **3** revealed that the hydrogen transfer is an intramolecular process and the Norrish type 1 cleavage is the rate-determining step ($K_H/K_D = 1.09 \pm 0.05$). Naphthalene was effective in quenching the photolysis of **1**, **2** and **3** at −70 °C, but quenching was incomplete at 5 °C. It was postulated that the two annulated benzene rings might circumscribe the carbonyl group by stereodynamic inversion and that the naphthalene molecule could not come close enough for the energy transfer.

Previously, it was reported[2,3] that 3,6-methanodibenzo[*a,f*]-cyclodecen-15-one and the dinaphtho- and benzonaphtho-derivatives exist in a stereodynamic equilibrium between the two chair-boat forms at room temperature. From the measured ΔG value (10–15 kcal mol^{-1}), it was suggested that the inversion between **C–B** and **B–C** is a stepwise process occurring *via* an intermediate twin-chair conformer, **T–C** (Scheme 1).



Scheme 1.

The Norrish type 1 photochemical cleavage[4] of ketones has been well studied for open chain and monocyclic ketones. An acyl–alkyl biradical generated from a cyclic ketone usually undergoes several competitive reactions, producing a mixture of various types of products (Scheme 2). However, the photochemistry of the bicyclic ketone system has been less investigated.[5–9] The only study of an aromatic ring-annulated methanocyclodecanone system, to our knowledge, reports on 6-methoxycarbonyl-5,6,7,8,9,10,11,12-octahydro-6,11-methanobenzocyclodecen-13-one.[10]



Scheme 2.

We herein report on the photochemistry of hexahydro-6,13-methanodibenzo[*a,f*]cyclodecen-15-ones **1**, **2** and **3**, from the viewpoint of product selectivity, kinetic isotope effect on the hydrogen transfer process after α-cleavage and the effect of wagging annulated benzene rings.

Results and Discussion

Preparation of **1–3** *and their Deuteriated Derivatives.*—Ketones **1** and **2** had been previously prepared.[2] Monoester **3** and deuteriated **2** and **3** were prepared according to Scheme 3. Partial hydrolysis of **1** using 10 equivs. of KOH in MeOH under reflux afforded the corresponding monocarboxylic acid **4** in 85% yield. Decarboxylation was carried out by heating **4** at 250 °C, giving **3** in 80% yield. Mono- and di-deuteriated compounds, [$^2H_1$]**2**, [$^2H_2$]**2** and [$^2H_1$]**3** were prepared by a sequence of reactions: deuterium exchange of the corresponding acid with an excess of D_2O and the pyrolysis of the resultant deuteriated acids. The ^1H NMR spectra of the products revealed that scrambling of the deuterium atom to the benzylic position did not occur during the pyrolysis and the [$^2H_1$]**2**, [$^2H_2$]**2** and [$^2H_1$]**3** obtained are isotopically pure.

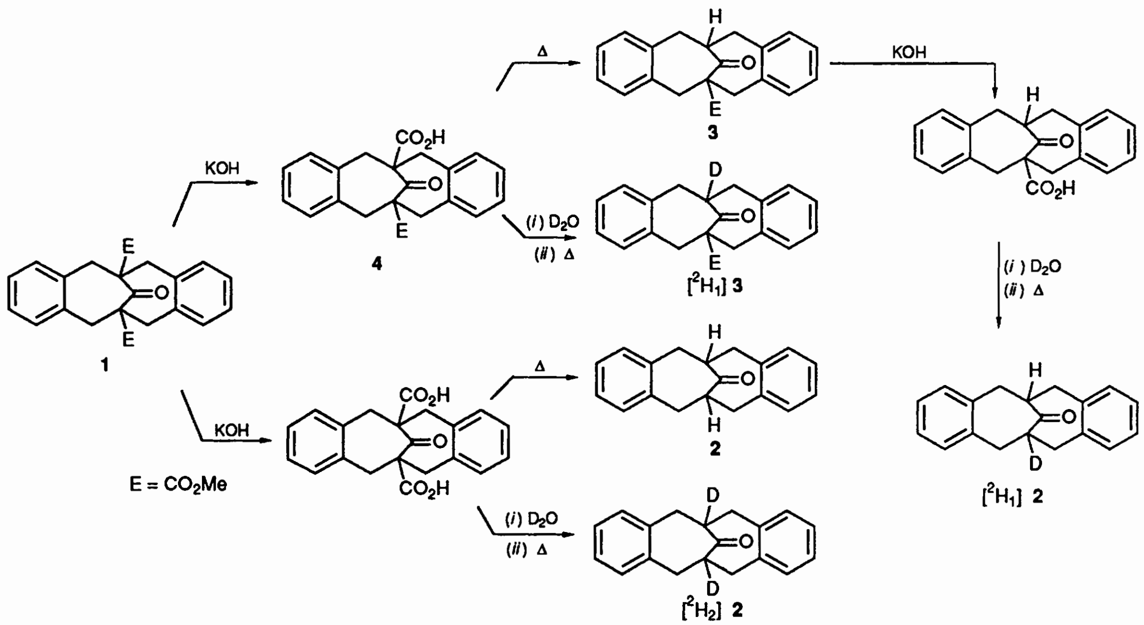
Photoreaction of **1–3**.—Acyl–alkyl biradicals generated from cyclic ketones by a Norrish-type 1 photoreaction usually undergo several competitive reactions such as coupling, disproportionation, rearrangement and cleavage, producing a mixture of various products. On the other hand, the photoreactions of **1**, **2** and **3** were product-selective as shown in Schemes 4 and 6.

When **1** was irradiated in degassed CH_2Cl_2, an *E–Z* mixture of the exclusive product **5** was obtained. The stereochemistry of **5** was determined on the basis of ^1H NMR spectra.

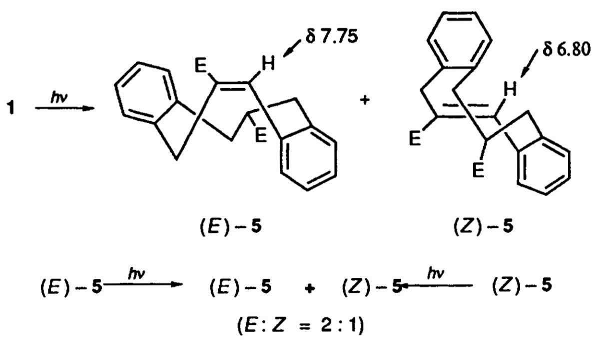
The relative ratio of *E*-**5**/*Z*-**5** changed from 7:1 after 0.5 h to 2:1 after 6 h during the photoreaction of **1**. Irradiation of both *E*-**5** and *Z*-**5** for 2 h gave the same 2:1 mixture of *E*-**5** and *Z*-**5**. These results indicate that *E*-**5** was formed first, isomerized, and then photochemically equilibrated with *Z*-**5** in the above photoreaction of **1**. Scheme 5 shows the pathway for formation of **5**. Irradiation caused the cleavage of the carbon–carbon bond between the bridge carbonyl carbon and the α-carbon in **1**, giving diradical **A-1**. The unpaired electron on the bridgehead position in **A-1** was stabilized by the ester function. Loss of CO and the 1,5-hydrogen shift of the resulting diradical, **B**, lead to a medium-sized cycloalkene *E*-**5**.

The photoreaction of **1** showed no solvent effect (CH_2Cl_2, dioxane and MeCN). Interestingly, the reaction was not quenched by triplet quenchers such as naphthalene, penta-1,3-diene, anthracene and perylene, for reasons discussed further on.

The photolysis of **2** (30 mmol) in CH_2Cl_2 at 5 °C and quenching of the photolysate with anhydrous MeOH gave the ester derivative **6** as the sole product. When the photolysate was quenched with dry air, ketone **7** was produced. The quenching with H_2O afforded a mixture of **8** and **9** (Scheme 6). These products could be derived from the ketone **10a**. Diradical **A-2** has no radical-stabilizing substituent on the bridgehead



Scheme 3.



Scheme 4.

position. Therefore, a transannular intramolecular hydrogen transfer[11,12] preceded the decarbonylation, giving ketene **10a** which, upon quenching with MeOH, produced **6**.

Photolysis of asymmetric **3** gave similar results to those of **2**. Quenching of the photolysate of **3** with MeOH gave a mixture of two stereoisomers, *cis*-**11** and *trans*-**11**, which were derived from the ketene **10b**. The conformational assignment of the two isomers was based on the NMR spectra; the spectrum of *cis*-**11** at −50 °C showed two methyl protons as one single peak (δ 3.89) but that of *trans*-**11** showed these as two singlet peaks (δ 3.85 and 3.90, respectively). Asymmetric **3** was expected to give two kinds of diradical, A-3 and A′-3. The diradical A-3 seems to be favoured and the diester **11** was exclusively produced from A-3 *via* **10b**.

Table 1. Isotopic purity[a] of reactants and products in the photolysis of a mixture of **2** and [$^2H_2$]**2**.

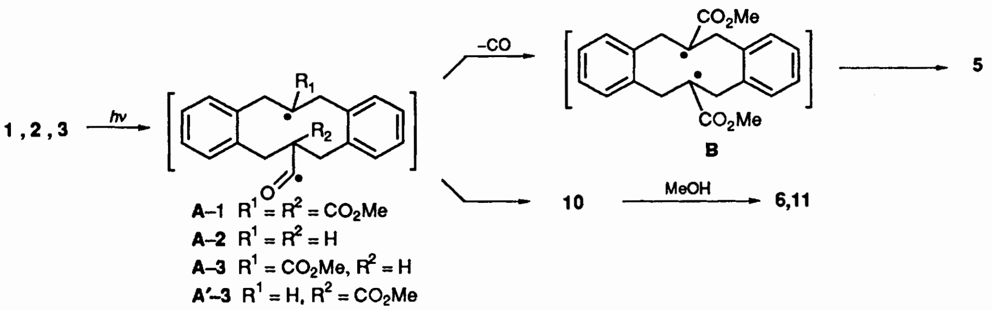
Reactant		Recovered		Product	
2	[$^2H_2$]**2**	**2**	[$^2H_2$]**2**	**6**	[$^2H_2$]**6**
0	90	0	88	0	89

[a] Determined by mass spectroscopy.

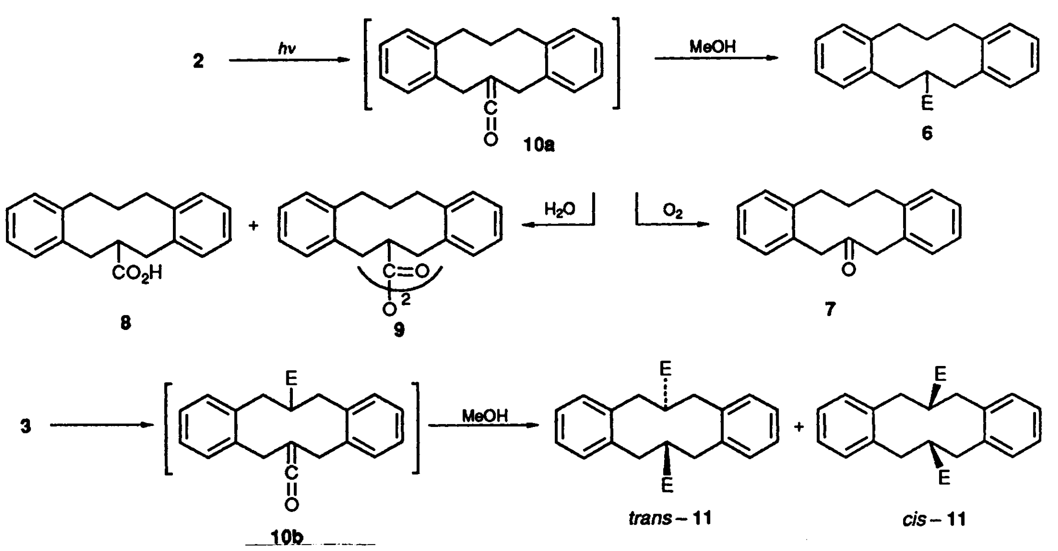
Photolysis of Deuteriated Derivatives.—The bridgehead deuteriated [$^2H_1$]**2**, [$^2H_2$]**2** and [$^2H_1$]**3** were irradiated to determine whether the hydrogen transfer is an intra- or an intermolecular process (Scheme 7). All deuterium atoms in the photoproducts, [$^2H_1$]**6**, [$^2H_2$]**6**, *cis*-[$^2H_1$]**11** and *trans*-[$^2H_1$]**11** exist on the bridgehead position and the deuterium contents of the products are as high as those of the starting [$^2H_1$]**2**, [$^2H_2$]**2** and [$^2H_1$]**3**.

A 1:1 mixture of **2** and [$^2H_2$]**2** was irradiated in order to investigate the possibility of hydrogen transfer among radical molecules trapped in the solvent cage. The deuterium contents and purities of the products, **6** and [$^2H_2$]**6**, and recovered starting materials were analysed by mass spectroscopy. The results in Table 1 indicate that the hydrogen transfer in the photolysis of **2** and **3** is an intramolecular process.

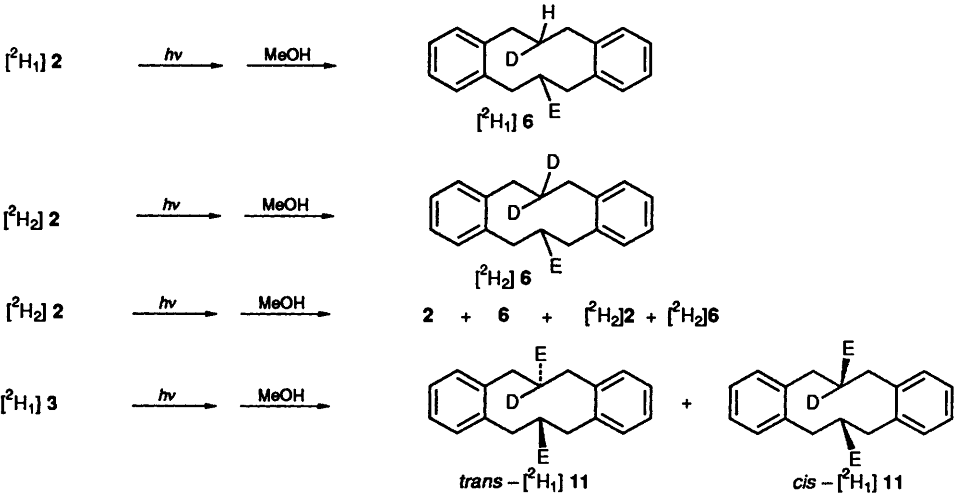
The isotope effect on the photolysis of **2**, [$^2H_1$]**2** and [$^2H_2$]**2** was studied using a 'merry-go-round' apparatus. The reaction rate was measured by VPC analysis of the photolysate



Scheme 5.



Scheme 6.



Scheme 7.

quenched by dry MeOH. Normal secondary kinetic α isotope effects were observed: $K_D/K_H = 1.09 \pm 0.05$ for $[^2H_1]$**2** and $K_D/K_H = 1.18 \pm 0.06$ for $[^2H_2]$**2**, respectively. (A secondary α-isotope effect of the order of 1.10–1.15 per deuterium has been reported for several homolytic reactions.[13]) This indicates that the rate-determining step is not the intramolecular hydrogen transfer step but the α-cleavage step producing diradical **A**.

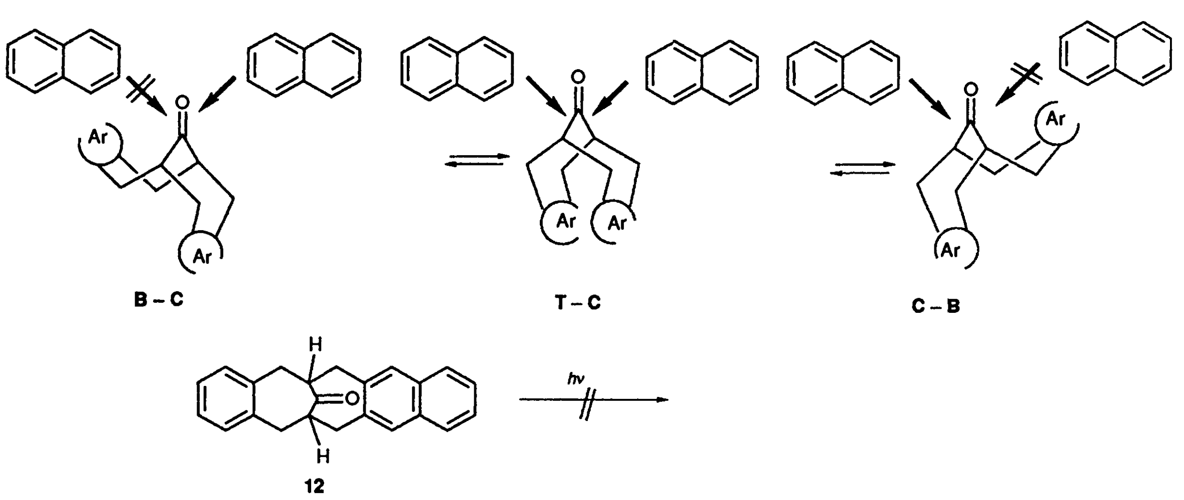
Stereodynamic Protection of the Carbonyl Group towards Triplet Quenchers by the Wagging Motion of Benzene Rings.— As previously mentioned, naphthalene, which has been frequently employed as a quencher in the photolysis of a variety of carbonyl compounds,[14] was not effective in the photolysis of **1**, **2** and **3**. For example, **6** was formed in the photolysis of **2** (1 h) in 39% relative yield in the absence of the quencher and in 30% yield in the presence of naphthalene (200 mol%).

As **2** inverts between the two equivalent chair–boat conformers at room temperature (Scheme 1), it was predicted that the wagging benzo group might circumscribe the carbonyl group and that the naphthalene molecule could not come close enough for the energy transfer from the excited carbonyl group to the naphthlene molecule. To support this theory, the following experiments were done: (*i*) photolysis of **1**, **2** and **3** at a low temperature such that inversion is prevented or slowed down, and (*ii*) photolysis of **12** bearing an intramolecularly incorporated naphthalene ring. The results are given in Table 2.

Photolysis of **2** was carried out at −70 °C in the absence of naphthalene. Product **6** was obtained in 37% relative yield after quenching with MeOH, indicating a small temperature effect in the photolysis. At −70 °C, naphthalene worked effectively as a quencher by approaching the photo-excited carbonyl group from the open site in the fixed chair–boat conformation of **2**, resulting in the quantitative recovery of **2**. Compounds **1** and **3** gave similar results (Table 2). However, the photolysis of the benzonaphtho compound **12** did not give any products at −70 °C or room temperature, and **12** was recovered quantitatively, as expected, due to an intramolecular energy transfer from the photo-excited carbonyl group to the annulated naphthalene in **12** (Scheme 8).

Experimental

M.p.s were determined on a Yanagimoto micro-melting point apparatus and are uncorrected. IR spectra were recorded on a Nippon Bunko A-102 spectrophotometer using KBr pellets. ^{1}H NMR spectra were taken on a Jeol FX-100, in $CDCl_3$, using $MeSi_4$. Mass spectra were recorded on a Nippon Denshi JMS-01SG-2 mass spectrometer at 75 eV using a direct-inlet system.



Scheme 8.

Table 2. Quenching experiment using naphthalene in the photolysis of **1**, **2** and **3**.

Reactant	Conditions[a,b]		Ratio[c] of product:reactant
	T/°C		
1	5	A	**5**:**1** = 19:81
1	5	B	**5**:**1** = 19:81
1	−70	A	**5**:**1** = 14:86
1	−70	B	**5**:**1** = 2:98
2	5	A	**6**:**2** = 39:61
2	5	B	**6**:**2** = 30:70
2	−70	A	**6**:**2** = 37:63
2	−70	B	**6**:**2** = 0:100
3	5	A	**11**:**3** = 23:77
3	5	B	**11**:**3** = 16:84
3	−70	A	**11**:**3** = 20:80
3	−70	B	**11**:**3** = 1:99

[a] Irradiation time: 1 h. [b] A: in the absence of naphthalene. B: in the presence of naphthalene (200 mol% of the reactant). [c] Determined by VPC.

VPC was done on Yanaco G-2800 gas chromatograph. Column chromatography was carried out on silica gel (WaKo gel, C-300). The light source for irradiation was a 100-W high-pressure Hg lamp (UVL-100HA, Riko-sha, Japan). All solvents used for the photoreaction were purified by standard procedures prior to use.

Preparation of 6-*Methoxycarbonyl*-5,6,7,12,13,14-*hexahydro*-6,13-*methanodibenzo*[a,f]*cyclodecen*-15-*one* **3**.—(i) *Partial hydrolysis of* **1**. A mixture of **1** (2.69 g, 7.12 mmol), potassium hydroxide (1.99 g, 35.6 mmol) and dimethyl sulphoxide (10 cm^3) in methanol (90 cm^3) was refluxed for 1 h. The reaction mixture was poured into water (150 cm^3), acidified with dilute hydrochloric acid, and left to stand overnight. The precipitates were collected by filtration are recrystallized from ethanol to give 13-methoxycarbonyl-15-oxo-5,6,7,12,13,14-hexahydro-6,13-methanodibenzo[*a,f*]cyclodecene-6-carboxylic acid **4** (2.20 g, 85%) as colourless *plates*, m.p. 252–254 °C (decomp.); δ_H 2.65–3.70 (m, 8 H), 3.72 (s, 3 H), and 7.00–7.45 (m, 8 H); ν/cm^{-1} 3250–2500, 1740, 1713, 1695 and 745; *m/z* 364 (M^+) (Found: C, 72.0; H, 5.8. $C_{22}H_{20}O_5$ requires C, 72.51; H, 5.53).

(ii) *Decarboxylation of* **4**. Compound **4** (2.20 g) was heated at 250 °C until gas evolution ceased and the pyrolysate was extracted with methylene chloride (50 cm^3). The extract was passed through a short silica gel column to remove coloured impurities and tar, then evaporated *in vacuo*. The residue, on recrystallization from ethanol, gave **3** (1.55 g, 80%) as colourless *prisms*, m.p. 160–162 °C; δ_H 2.59–3.12 (m, 9 H), 3.67 (s, 3 H), and 6.93–7.23 (m, 8 H); ν/cm^{-1} 2948, 1737, 1697 and 749; *m/z* 320 (M^+) (Found: C, 78.6; H, 6.4. $C_{21}H_{20}O_3$ requires C, 78.72; H, 6.29).

6-*Deuterio*-13-*methoxycarbonyl*-5,6,7,12,13,14-*hexahydro*-6,13-*methanodibenzo*[a,f]*cyclodecen*-15-*one* [$^2H_1$]**3**.—A mixture of **4** (320 mg, 0.88 mmol), [$^2H_1$]methyl alcohol (9 cm^3), hexadeuteriodimethyl sulphoxide (1 cm^3) and deuterium oxide (0.2 cm^3) was stirred at room temperature for 5 min, then evaporated *in vacuo*. The residue was heated at 250 °C until no gas was evolved. The pyrolysate was worked up as for **3**, giving [$^2H_1$]**3** (0.23 g, 82%) as colourless *prisms*, m.p. 160–162 °C (ethanol); δ_H 2.63–3.14 (m, 8 H), 3.67 (s, 3 H) and 6.93–7.23 (m, 8 H); ν/cm^{-1} 2946, 1736, 1695 and 747; *m/z* 321 (M^+) (Found: C, 78.3; H, 6.7. $C_{21}H_{19}[^2H_1]O_3$ requires C, 78.49; H, 6.58).

6,13-*Dideuterio*-5,6,7,12,13,14-*hexahydro*-6,13-*methanodibenzo*[a,f]*cyclodecen*-15-*one* [$^2H_2$]**2**.—A mixture of 15-oxo-5,6,7,12,13,14-hexahydro-6,13-methanodibenzo[*a,f*]cyclodecene-6,13-dicarboxylic acid (1.28 g, 3.65 mmol), [$^2H_1$]methyl alcohol (5 cm^3), hexadeuteriodimethyl sulphoxide (2 cm^3) and deuterium oxide (1 cm^3) was treated as described above and pyrolysed at 330 °C. The pyrolysate was worked up as for **3**, giving [$^2H_2$]**2** (0.77 g, 80%) as colourless *prisms*, m.p. 132–135 °C (ethanol); δ_H 2.83 (br s, 8 H) and 7.15 (br s, 8 H); ν/cm^{-1} 2936, 1698 and 745; *m/z* 264 (M^+) (Found: C, 86.5; H, 7.5. $C_{19}H_{16}[^2H_2]O$ requires C, 86.32; H, 7.63).

6-*Deuterio*-5,6,7,12,13,14-*hexahydro*-6,13-*methanodibenzo*-[a,f]*cyclodecen*-15-*one* [$^2H_1$]**2**.—(i) *Hydrolysis of* **3**. A mixture of **3** (1.07 g, 3.34 mmol) and potassium hydroxide (3.00 g, 53.6 mmol) in methanol (30 cm^3) was refluxed for 1.5 h, then poured into water (30 cm^3) and acidified with dilute hydrochloric acid. The precipitate was filtered and recrystallized from methanol to give 15-oxo-5,6,7,12,13,14-hexahydro-6,13-methanodibenzo-[*a,f*]cyclodecene-6-carboxylic acid (0.97 g, 95%) as colourless *plates*, m.p. 265–267 °C (decomp.); δ_H 2.60–3.30 (m, 9 H) and 6.95–7.40 (m, 8 H); ν/cm^{-1} 3400–2800, 1728, 1686 and 756; *m/z* 306 (M^+) (Found: C, 78.8; H, 5.6. $C_{20}H_{18}O_3$ requires C, 78.41; H, 5.92).

(ii) *Pyrolysis*. A mixture of the above prepared carboxylic acid (620 mg, 2.03 mmol), [$^2H_1$]methyl alcohol (10 cm^3), hexadeuteriodimethyl sulphoxide (3 cm^3) and deuterium oxide (1 cm^3) was stirred for 5 min at room temperature and evaporated *in vacuo*. The residue was pyrolysed at 240 °C, and the pyrolysate was worked up as for **3**, giving $[^2H_1]$**2** (0.43 g, 80%) as colourless *prisms*, m.p. 132–135 °C (ethanol); δ_H 2.83 (br s, 8 H), 3.07–3.17 (quin, *J*/Hz 7, 1 H), and 7.15 (br s, 8 H); ν/cm^{-1} 2938, 1700 and 746; *m/z* 263 (M^+) (Found: C, 87.0; H, 7.25. $C_{19}H_{17}[^2H]O$ requires C, 86.65; H, 7.27).

Photolysis of **1**.—A 30 mmol solution (60 cm^3) of **1** in dry methylene chloride was purged with N_2 and irradiated through a Pyrex filter for 6 h at 5 °C. The photolysate gave a 40:40:20 mixture of **1**, *E*-**5** and *Z*-**5** by VPC. The slightly yellow solution was filtered through silica gel to remove coloured impurities and tar. The filtrate was evaporated *in vacuo*, yielding a residue which was recrystallized from ethanol to give **1** (0.25 g), *E*-**5** (0.23 g) and *Z*-**5** (0.11 g) in this sequence.

6-*Methoxycarbonyl*-(E)-5,6,7,12-*tetrahydrodibenzo*[a,f]-*cyclodecene E*-**5**. Colourless *prisms*, m.p. 109.5–110.5 °C (ethanol); δ_H 2.35–3.90 (m, 7 H), 3.80 (s, 6 H), 6.80–7.45 (m, 8 H), and 7.75 (s, 1 H); ν/cm^{-1} 2950, 1715 and 751; *m/z* 350 (M^+) (Found: C, 75.25; H, 6.25. $C_{22}H_{22}O_4$ requires C, 75.41; H, 6.33).

6-*Methoxycarbonyl*-(Z)-5,6,7,12-*tetrahydrodibenzo*[a,f]-*cyclodecene Z*-**5**. Colourless *prisms*, m.p. 123.5–124.5 °C (ethanol); δ_H 2.65–4.00 (m, 7 H), 3.35 (s, 3 H), 3.65 (s, 3 H), 6.87 (s, 1 H), and 7.05–7.25 (m, 8 H); ν/cm^{-1} 2952, 1730 and 757; *m/z* 350 (M^+) (Found: C, 75.55; H, 6.3. $C_{22}H_{22}O_4$ requires C,75.41; H, 6.33).

Photolysis of **2**.—A 30 mmol solution (60 cm^3) of **2** in dry methylene chloride was irradiated as described for the photolysis of **1** for 6 h. The photolysate was quenched with dry methanol (2 cm^3). The mixture was worked up as described for **1** and recrystallized from ethanol to give 6-methoxycarbonyl-5,6,7,12,13,14-hexahydrodibenzo[*a,f*]cyclodecene **6** (318 mg, 60%) as colourless *prisms*, m.p. 142–144 °C; δ_H 2.02–2.34 (m, 2 H), 2.30–3.15 (m, 8 H), 3.16–3.28 (quin, 1 H), 3.85 (s, 3 H), and 7.0–7.3 (m, 8 H); ν/cm^{-1} 2912, 1734 and 749; *m/z* 294 (M^+) (Found: C, 81.20; H, 7.55. $C_{20}H_{22}O_2$ requires C, 81.60; H, 7.53). From the mother liquor, unchanged **2** was recovered (169 mg, 36%).

Quenching of the photolysate with dry air gave **7**, and quenching with water gave **8** and **9**.

6-*Oxo*-5,6,7,12,13,14-*hexahydrodibenzo*[a,f]*cyclodecene* **7**. Colourless prisms, m.p. 146–148 °C (ethanol); δ_H 2.15–2.35 (m, 2 H), 2.35–2.65 (m, 4 H), 3.40–3.70 (m, 4 H), and 6.95–7.40 (m, 8 H); ν/cm^{-1} 2964, 1707 and 747; *m/z* 250 (M^+) (Found: C, 86.65; H, 7.05. $C_{18}H_{18}O$ requires C, 86.36; H, 7.25).

5,6,7,12,13,14-*Hexahydrodibenzo*[a,f]*cyclodecene*-6-*carboxylic acid* **8**. Colourless needles, m.p. 205 °C (decomp.) (ethanol); δ_H 2.00–3.40 (m, 11 H) and 7.10–7.33 (m, 8 H); ν/cm^{-1} 3300–2500, 1700 and 750; *m/z* 280 (M^+) (Found: C, 81.15; H, 7.2. $C_{19}H_{20}O_2$ requires C, 81.39; H, 7.19).

5,6,7,12,13,14-*Hexahydrodibenzo*[a,f]*cyclodecene*-6-*carboxylic anhydride* **9**. White needles, m.p. 181–182 °C (benzene); δ_H 1.40–1.70 (m, 4 H), 2.00–3.15 (m, 16 H), 3.35–3.50 (m, 2 H), and 7.05–7.50 (m, 16 H); ν/cm^{-1} 1812, 1748 and 750; *m/z* 542 (M^+) (Found: C, 83.85; H, 6.90. $C_{38}H_{38}O_3$ requires C, 84.10; H, 7.06).

Photolysis of **3**.—A 30 mmol solution (60 cm^3) of **3** in dry methylene chloride was irradiated as above for 6 h and quenched with dry methanol. The reaction mixture was worked up as for **2** and recrystallized from ethanol to give *trans*-**11** (0.19 g, 30%) and *cis*-**11** (0.19 g, 30%). Unchanged **3** (220 mg, 38%) was recovered from the mother liquor.

trans-6,13-*Dimethoxycarbonyl*-5,6,7,12,13,14-*hexahydrodibenzo*[a,f]*cyclodecene* trans-**11**. Colourless needles, m.p. 146–148 °C; δ_H 2.65–3.45 (m, 10 H), 3.84 (s, 6 H), and 6.60–7.30 (m, 8 H); ν/cm^{-1} 2984, 1730 and 747 (Found: M^+ 352.1675. $C_{22}H_{24}O_4$ requires *M* 352.1673).

cis-6,13-*Dimethoxycarbonyl*-5,6,7,12,13,14-*hexahydrodibenzo*[a,f]*cyclodecene* cis-**11**. Colourless plates, m.p. 260–262 °C; δ_H 2.60–3.10 (m, 8 H), 3.25–3.35 (quin, 2 H), 3.84 (s, 6 H), and 6.95–7.25 (m, 8 H); ν/cm^{-1} 2946, 1732 and 757 (Found: M^+ 352.1676. $C_{22}H_{24}O_4$ requires *M* 352.1673).

Determination of the Kinetic Isotope Effect.—Five samples of a 30 mmol dry methylene chloride solution (0.60 cm^3) of **2**, $[^2H_1]$**2** and $[^2H_2]$**2**, respectively, were prepared in 5 × 180 mm Pyrex tubes. These samples were deoxygenated by bubbling nitrogen for 10 min, then sealed and irradiated in a 'merry-go-round' apparatus immersed in a water bath (5 °C). Every 5 min, one sample was taken out and quenched with dry methanol (0.05 cm^3). The ratio of the products and unchanged starting materials were determined by VPC (glass capillary column, 25 m, silicon OV-1701).

Quenching of the Photolyses of **1**, **2**, **3** *and* **12**.—Five samples of a 30 mmol dry methylene chloride solution (0.60 cm^3) of the substrate in a Pyrex tube (5 × 180 mm) were prepared. Another five samples with additional naphthalene (200 mol% of the reactant) were also prepared. All samples were deaerated by bubbling oxygen-free nitrogen for 10 min, then sealed and irradiated for 1 h at 5 or −70 °C. The reaction mixtures of **2** and **3** were quenched with dry methanol (0.05 cm^3) after photolysis. Each photolysate was analysed by VPC (glass capillary column, 25 m, silicon OV-1701).

Acknowledgements

We are grateful to Professor Taku Matsuo of Kyushu University for the use of a 'merry-go-around' apparatus for the photoreactions.

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Paper 0/02884C
Received 26*th June* 1990
Accepted 24*th July* 1990