Furan-2(3*H*)- and -2(5*H*)-ones. Part 6.[1] Di-π-methane rearrangement of the α-substituted 4-benzylfuran-2(5*H*)-one system[2]

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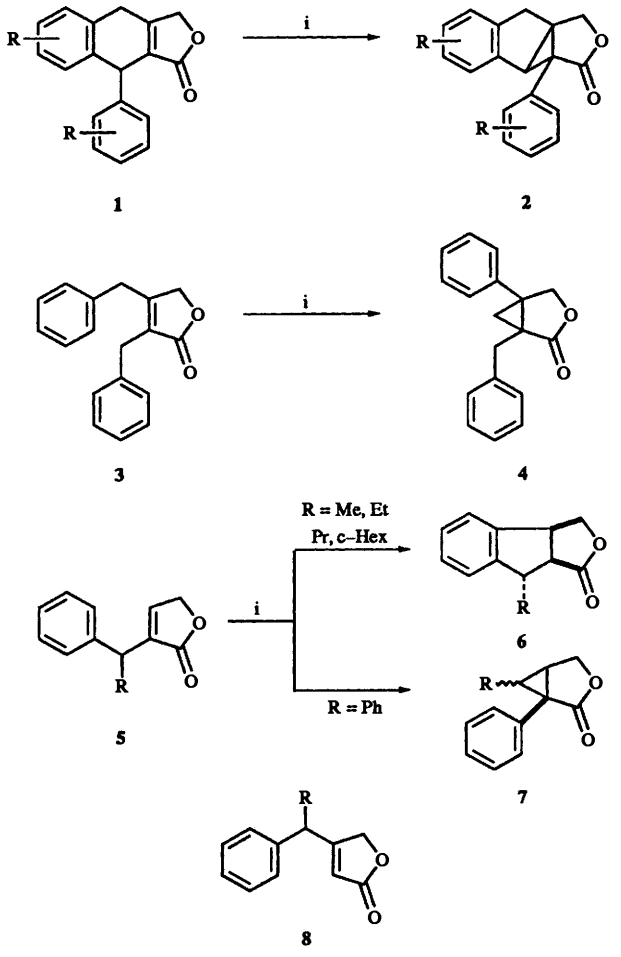
The effect of the 'central methane' substitution on the di-π-methane rearrangement in 4-benzyl-2,5-dihydrofuran-2-ones **8a–d** was investigated. Significant enhancement of efficiency in the rearrangement leading in high combined yields to two isomeric products, *endo*-**12** and *exo*-**12**, is discussed in terms of both the substituent effects at the benzylic carbon and the restrained features of the ring-enrolled π-system. The origin of the difference in chemoselectivity compared with that of the 3-benzyl counterpart **5** where a photoarylated product **6** resulted upon photoirradiation was also investigated, and was rationalized by postulating a higher reactivity at the β-position of the enone system.

Introduction

It is well known that photoirradiation of molecules having the di-π-methane moiety, *i.e.*, having two π-systems bound to a single sp^3 carbon, causes rearrangement to give π-substituted cyclopropanes. The reaction was termed the di-π-methane rearrangement, and intensive work on its mechanistic and other features has been reported by Zimmerman and co-workers.[3]

In a previous paper, we reported the regiospecific di-π-methane rearrangement of β-apolignans **1** into the corresponding tetrahydrocyclopropa[*a*]indenes **2**, and revealed that the rearrangement is common among β-apolignans irrespective of their ring substituents and that only the pendant phenyl group migrates among the three possible di-π-methane systems found in the β-apolignans.[4] On the other hand, upon irradiation of 3,4-dibenzyl-2,5-dihydrofuran-2-one **3**, a system lacking the stereochemical rigidity of compounds **1** reverse selectivity of migration was observed, affording a cyclopropano lactone **4** as the main product.[2a,5] In a further study on the photoreactivity of the aryl(butenolidyl)methane system, monobenzyl analogues, 3-benzyl-2,5-dihydrofuran-2-ones **5** (R = H, Me, Et, Pr, c-Hex) were examined, where characteristic photoarylation leading to the corresponding tetrahydroindenofuranones **6** (R = Me, Et, Pr, c-Hex) was found to occur with the introduction of substituents on the 'central methane' carbon,[1,6] and only the phenyl-substitution substrate (**5**; R = Ph) to result in the di-π-methane rearrangement, affording a cyclopropano lactone **7** (R = Ph) in moderate yield. Thus, it was of considerable interest to study the photochemical behaviour of their 4-benzyl counterparts, 4-benzyl-2,5-dihydrofuran-2-ones **8** (R = H, Me, c-Hex, Ph), from both the quantitative and mechanistic viewpoints, in order to understand the difference in chemo- and regio-selectivity observed among these three types of benzyl-2,5-dihydrofuran-2-one **1**, **3** and **5** (Scheme 1).



a; R = H; **b**; R = Me; **c**; R = c-Hex; **d**; R = Ph

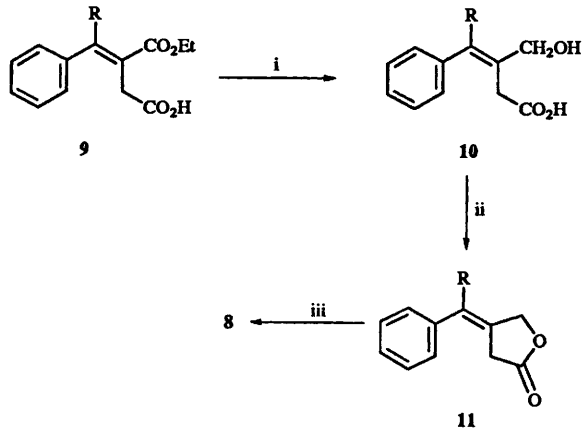
Scheme 1 *Reagents and conditions:* i, *hv*. c-Hex is cyclohexyl.

Results

Synthesis of 4-(α-substituted benzyl)-2,5-dihydrofuran-2-ones 8a–d and 5-phenyl-3-oxabicyclo[3.1.0]hexan-2-one 12a

4-Benzyl-2,5-dihydrofuran-2-one **8a** was synthesized as follows. The selective reduction of 1-ethyl 4-hydrogen 2-benzylidenesuccinate **9a**[7] with lithium aluminium hydride (LAH) at −10–0 °C followed by successive lactonization and isomerization[8] of the resulting hydroxy acid, 3-hydroxymethyl-4-phenylbut-3-enoic acid **10a**, by the action of hydrochloric acid gave the desired furanone **8a**[9] in 65% overall yield from starting material **9a**.

The 'central methane'-substituted analogues **8b–d** were prepared starting from the corresponding 1-ethyl 4-hydrogen 2-benzylidenesuccinates **9b–d** in 43–61% overall yield, where isomerization of compounds **11b–d** to compounds **8b–d** was carried out by treatment with tosic acid (PTSA) in dimethyl

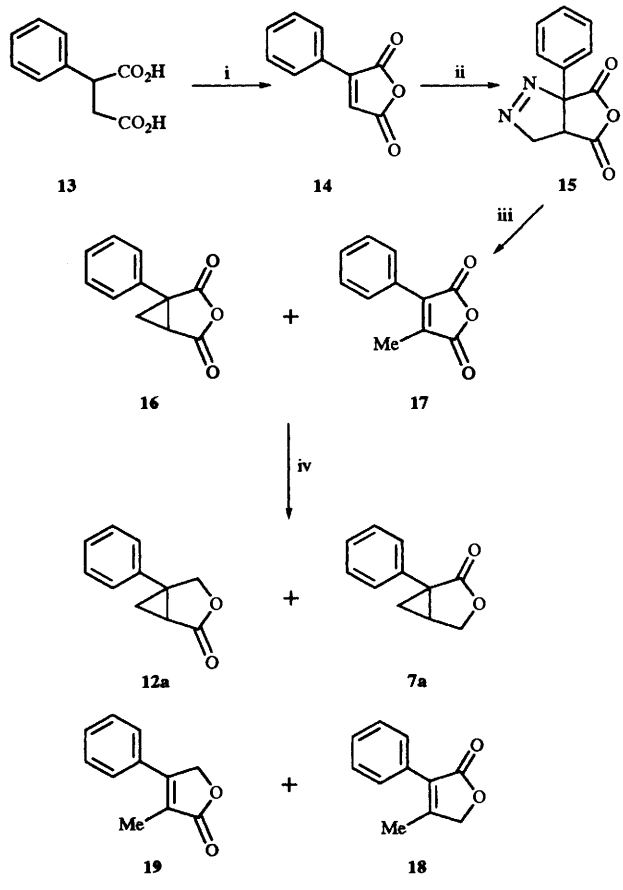


Scheme 2 *Reagents and conditions:* i, $LiAlH_4$; ii, 10% HCl or 10% H_2SO_4; iii, PTSA, DMSO, 150 °C

sulfoxide (DMSO) at 150 °C, because attempted isomerization with hydrochloric acid gave a complex mixture (Scheme 2).

The IR spectra of the products **8a–d** showed absorptions at 1746–1785 cm^{-1} and 1632–1639 cm^{-1} due to the α,β-unsaturated γ-lactone system. Signals at δ_H 5.71–5.99 and at δ_C 115.1–118.6, in the ^1H and ^{13}C NMR spectra, respectively, were in accord with the structure of β-substituted 2,5-dihydrofuran-2-ones.

An authentic sample of 5-phenyl-3-oxabicyclo[3.1.0]hexan-2-one **12a**, a product predicted to form upon photoirradiation of compound **8a**, was synthesized as shown in Scheme 3. 2-Phenylsuccinic acid **13** was converted into 2-phenylmaleic anhydride **14** according to the method by Hill.[10] Treatment of anhydride **14** with diazomethane followed by thermal elimination of nitrogen[11] from the resulting 1-pyrazoline **15** afforded a 3:1 mixture of 1-phenyl-3-oxabicyclo[3.1.0]hexane-2,4-dione **16**[12] and 2-methyl-3-phenylmaleic anhydride **17**.[13] The mixture was treated, without fractionation, with sodium boranuide to give four lactones, 1-phenyl-3-oxabicyclo-[3.1.0]hexan-2-one **7a**,[12b,14] the desired lactone **12a**,[14b] 4-methyl-3-phenyl-2,5-dihydrofuran-2-one **18**,[9b,15] and 3-methyl-4-phenyl-2,5-dihydrofuran-2-one **19**[16] in 37, 18, 10 and 7% yield from compound **15**, respectively.



Scheme 3 *Reagents and conditions:* i, Ac_2O, SeO_2; ii, CH_2N_2; iii, PhH, 70 °C; iv, $NaBH_4$

The spectral properties of the major cyclopropano lactone **7a** were in good accord with those previously reported.[14a] The ^1H NMR spectrum of the minor cyclopropano lactone displayed a pair of one-proton doublets of doublets at δ_H 1.38† and δ_H 1.70 due to the cyclopropane methylene protons. Signals due to the lactonic γ-methylene moiety appeared as a pair of one-proton doubles at δ_H 4.47 and δ_H 4.50 while those of the major isomer **7a** appeared as a one-proton doublet and a one-proton doublet of doublets at δ_H 4.29 and δ_H 4.46, respectively. Thus, the minor isomer was identified as the desired compound **12a**.

Photoirradiation of 4-(α-substituted benzyl)-2,5-dihydrofuran-2-ones 8a–d

Direct irradiation of compound **8a** in methanol through a Pyrex filter for 12 h gave compound **12a**, a photoreduced product, 4-benzyltetrahydrofuran-2-one **20**,[17] and a solvent adduct, 4-benzyl-4-(hydroxymethyl)tetrahydrofuran-2-one **21**, in 39, 15 and 8% yield, respectively, with recovery of the starting material (33%). Additionally, formation of a trace amount of another solvent adduct, 4-benzyl-3-(hydroxymethyl)tetrahydrofuran-2-one **22**, was also detected. Prolonged irradiation caused the degradation of compound **12a** to give a cyclopropano ester, methyl *trans*-2-hydroxymethyl-2-phenylcyclopropane-1-carboxylate **23**, as an additional product. The photodegradation of compound **12a** to ester **23** was evidenced by the independent irradiation of compound **12a** in methanol.‡

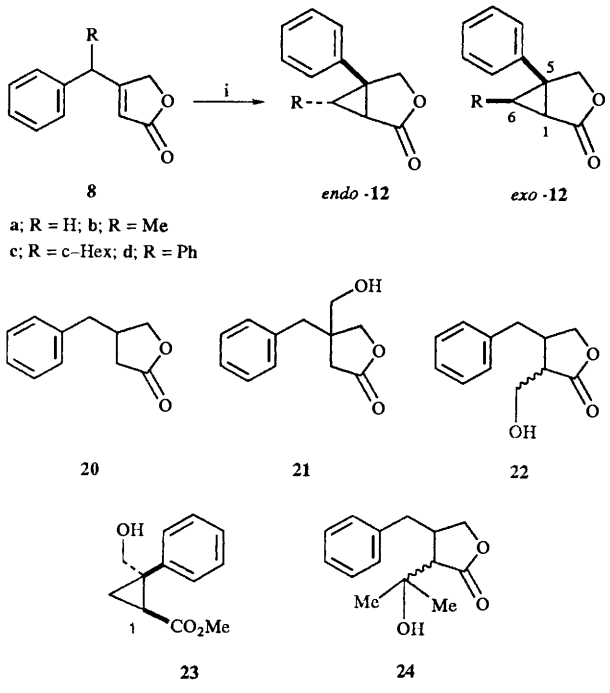
Acetone-sensitized irradiation of compound **8a** under the same conditions as those of the run in methanol gave compounds **12a** and **20**, and a solvent adduct, 4-benzyl-3-(2-hydroxypropan-2-yl)tetrahydrofuran-2-one **24** in 47, 10 and 13% yield, respectively. These reactions are shown in Scheme 4.

The cyclopropano lactone **12a** was identical with an authentic specimen synthesized *via* an alternative route, and the photoreduced product **20** with the one obtained by the hydrogenation of compound **8a**.

The IR spectrum of the methanol adduct **21** showed absorptions due to the hydroxy group and lactone carbonyl at 3450 and 1771 cm^{-1}, respectively. Its ^1H NMR spectrum displayed a singlet at δ_H 3.54 due to carbinol protons. A singlet at δ_C 45.6 and four triplets at δ_C 36.3, 39.7, 64.8 and 73.9 in the ^{13}C NMR spectrum are in accord with its assigned structure. Moreover, compound **21** displayed a peak due to the molecular ion at *m/z* 206 (17%) in the mass spectrum.

† The assignment of the signal in a previous communication (ref. 2*a*) was found to be incorrect and was corrected on the basis of a ^{13}C–^1H COSY experiment in the present study.

‡ The formation of ester *trans*-**23** would be attributed to the 1,5-bond cleavage of compound **12a** followed by ring closure of the ketene intermediate. The 1,5-bond cleavage of the 3-oxabicyclo[3.1.0]hexan-2-one system to form a ketene intermediate has been reported (ref. 18), and the cyclization, though ionic, of an α-enolate of a γ,δ-epoxycarbonyl compound into the α-carbonyl-substituted cyclopropanemethanol system has been reported (ref. 19). It is reasonable that the stereoisomer of compound *trans*-**23** could not be detected, because compound **12a** is found to be more stable than compound *cis*-**23** by the experiment where compound **12a** was not consumed to any extent in its acidic methanolysis.



Scheme 4 *Conditions:* i, *hν*

The structure of cyclopropano ester **23** was assigned on the basis of its IR band (C=O at 1722 cm^{-1}), ^1H NMR signals (cyclopropane CH_2 at δ_H 1.36 and 1.74† as a pair of doublets of doublets, O=CCH at δ_H 2.10† as a doublet of doublets, CH_2OH at δ_H 3.57 and 3.80 as a pair of doublets, and OMe at δ_H 3.43 as a singlet), and MS peaks [*m*/*z* 206 (M^+, 5%) and 91 (66%)]. A small vicinal coupling constant[20] of the deshielded signal at δ_H 1.74 (J_{trans} 5.5 Hz) due to one of the cyclopropane methylene protons suggested an inversion of the stereochemistry[21] on C-1, since in compound **12a** the corresponding *exo* proton (δ_H 1.70) displayed a larger value (J_{cis} 9.3 Hz). The relative stereochemistry of compound **23** was confirmed on the basis of differential nuclear Overhauser effect (NOE) experiments, where an NOE was observed between the methine proton and one of the methylene protons on the cyclopropane ring, and also between the aromatic *ortho* protons and another one of the ring-methylene protons. Moreover, no NOE enhancement was detected between the methine proton and the aromatic *ortho* protons.

The IR spectrum of acetone adduct **24** showed absorptions due to the hydroxy group and lactone carbonyl at 3450 and 1762 cm^{-1}, respectively. Its ^1H NMR spectrum displayed a pair of three-proton singlets, at δ_H 0.86 and 1.27, due to two methyl groups attached to the sp^3 carbon bearing a hydroxy group. A two-proton broad singlet at δ_H 3.76 corresponded to the lactonic γ-methylene moiety. However, the stereochemistry of compound **24** is not clear since the signals due to the benzylic methylene protons and the methine proton α to the carbonyl are undistinguishable in its ^1H NMR spectrum.

Direct irradiation of the 'central methane'-substituted systems **8b–d** in methanol afforded the corresponding products of di-π-methane rearrangement, *exo*- and *endo*-6-substituted 5-phenyl-3-oxabicyclo[3.1.0]hexan-2-ones, *exo*- and *endo*-**12b–d**, in 77–93% yield.

Upon acetone-sensitized irradiation, the rearrangement proceeded more efficiently, affording the same products, *exo*- and *endo*-**12b–d**, in a shorter reaction time. The formation of two diastereoisomers *exo*- and *endo*-**12** may be attributed to the readily occurring photoisomerization in the bicyclo[3.1.0]-hexane system,[22] because compounds **12** showed interconversion between the isomers upon irradiation. The results of the irradiation are summarized in Table 1.

In every case, the *endo*-isomer was the major product, and spectral properties of the rearrangement products **12b**, **12c** and **12d** were similar, and are suggestive of a cyclopropano lactone structure of the same type. The ^1H NMR spectrum of *endo*-**12c** displayed a one-proton doublet of doublets at δ_H 2.42 and a one-proton doublet of doublets at δ_H 1.59, due to two methine protons on C-1 and C-6, respectively. Although the coupling constant ($J_{1,6}$ 9.5 Hz) observed between the two vicinal protons on the cyclopropane ring suggested their *cis* relationship, the relative stereochemistry was confirmed on the basis of NOE experiments. A marked NOE observed between the two methine protons on the ring and another NOE between the methine proton on C-6 and aromatic *ortho* protons supported the *endo* orientation of the cyclohexyl group.

Meanwhile, the vicinal methine protons of the *exo*-isomer, *exo*-**12c**, appeared at δ_H 2.28 and 1.35, displayed a smaller coupling ($J_{1,6}$ 3.5 Hz), and no NOE was observed between these two protons, supporting their *trans* stereochemistry.

Discussion

Among the three versions of the di-π-methane rearrangement,[3] *viz.* the divinylmethane variety, the aryl-vinylmethane type and the oxa-di-π-methane variation,[23] the divinylmethane rearrangement requires substitution at the 'methane carbon' while the aryl-vinyl type does not.[24] Present findings show that the efficiency of the rearrangement increases also in the case of the aryl-vinyl version with introduction of substituents on the 'central carbon'.[25] Even monosubstitution on the 'central methane' carbon increased the efficiency of the rearrangement to a large extent, although a substituent effect on the central methane has mostly been demonstrated on disubstituted substrates.[25]

Most interestingly, contrasting photoreactivity was encountered in comparison with the case of the 3-benzyl counterpart **5**, where a characteristic photocyclization took place to give the corresponding tetrahydroindenofuranone **6** in good yield. The formation of a radical at the β-position, preferred to that at the position α to the carbonyl, would be responsible for the difference in chemoselectivity observed between these two regioisomers (Scheme 5).

Fasel and Hansen[26] reported the photoreaction of an allylbenzene, 1-(but-3-en-2-yl)-3,5-dimethylbenzene **25**, the simplest version of the 'cental methane'-substituted aryl-vinyl system without any contribution by carbonyl, where the efficiency of the reaction leading to cyclopropanes **26** was apparently inferior to the present case. Thus the contribution of the carbonyl group towards the enhancement of the reactivity is apparent (see Scheme 6).

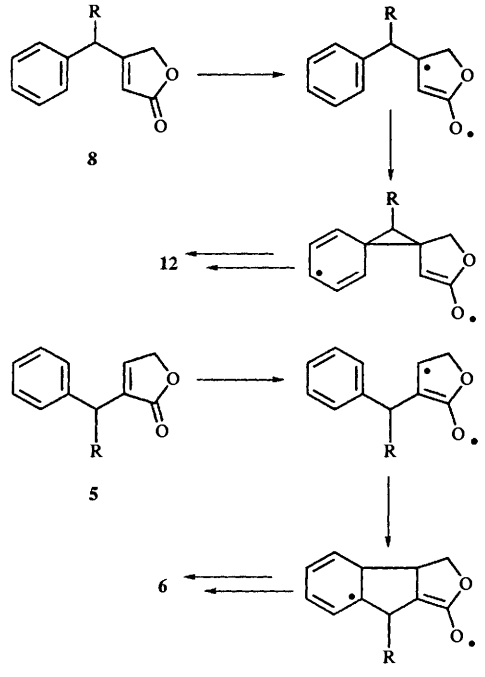
Photoirradiation of ethyl 4-methyl-4-phenylpent-2-enoate **27**, an acyclic substrate similar to compound **8a**, has also been reported. In this case, the di-π-methane rearrangement to yield the cyclopropano ester **28** could be effected only upon direct irradiation, but not on acetone-photosensitized irradiation.[27] Hixson[28] rationalized the non-occurrence of the di-π-methane reaction of the triplet excited state of compound **27** in terms of preferential dissipation of the triplet excitation energy by 'free-rotor' effects (easy *E*–*Z* isomerization)[29] about the double bond (see Scheme 6).

Consequently, preferential reactivity at the position β to the carbonyl in the conjugated enone system controls the chemoselectivity of the photoreaction. The efficiency of the rearrangement in the present study should be ascribed to both

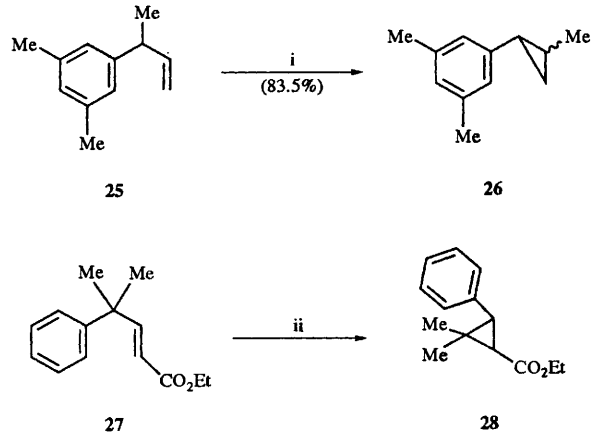
† See footnote on p. 1438.

Table 1

Substrate		Reaction		Products (isolated yield %)							
8	R	time (*t*/h)	Solvent	*endo*-**12**	*exo*-**12**	**20**	**21**	**22**	**23**	**24**	Recov'd
a	H	3	Me_2CO	47		6				13	7
		12	MeOH		39	15	8	Trace	Trace		33
		24	MeOH		18	11	13	Trace	7		
b	Me	6	Me_2CO	90	Trace						
		11	MeOH	70	7						
c	Cyclohexyl	8	Me_2CO	85	8						
		11	MeOH	74	19						
d	Ph	4	Me_2CO	70	15						
		11	MeOH	70	13						



Scheme 5



Scheme 6 *Conditions*: i, *hv*, 32.5 h; ii, *hv*

the effect of substitution at the 'central methane' carbon on enforcing its ready migration *via* radical fission and the inherent feature of the 2,5-dihydrofuran-2-one system where this alternative photoprocess (*E*–*Z* isomerization) is precluded by incorporating the double bond in a furanone ring. Regioselective rearrangement of the pendant phenyl in β-apolignans **1** could be attributable to the stereoelectronic requirements.[3] Further studies on the selectivity in the di-π-methane rearrangement of the aryl-butenolidyl-methane system from this viewpoint are in progress.

Experimental

Mps (Yanagimoto MP-3S micromelting point apparatus) and bps are uncorrected. IR spectra were measured on a Shimadzu IR-435 grating infrared spectrophotometer. NMR spectra were recorded on either a JEOL JNM-GSX 270 (270 MHz ^1H, 67.5 MHz ^{13}C) or a JEOL JNM-GSX 500 (500 MHz ^1H, 125 MHz ^{13}C) spectrometer. Chemical shifts and coupling constants (*J*) are given in δ-values (ppm) and in hertz (Hz), respectively. All the NMR spectra were taken for $CDCl_3$ solutions with tetramethylsilane as internal standard. Low-resolution mass and high-resolution mass spectra (electron impact) were recorded on either a Shimadzu QP 1000EX spectrometer or a JEOL JMS-HX 100 spectrometer. Column chromatography was effected over either Merck Kieselgel 60 (230–400 mesh) with a pump (FMI model RP) or Merck Kieselgel 60 (70–230 mesh). Photochemical reactions, except those in a test tube, were carried out under a stream of dry, oxygen-free nitrogen, through a Pyrex filter at 25 °C in an immersion apparatus fitted with an Ishii UV-HT 200 W high-pressure mercury lamp. All the organic extracts were dried over anhydrous magnesium sulfate prior to evaporation. Light petroleum refers to the fraction with distillation range 30–70 °C.

4-Benzyl-2,5-dihydrofuran-2-one 8a

A solution of 1-ethyl 4-hydrogen 2-benzylidenesuccinate[7] **9a** (9.0 g, 38.5 mmol) in tetrahydrofuran (THF) (60 cm^3) was added to a stirred suspension of LAH (1.46 g, 38.4 mmol) in THF (50 cm^3) at −10 °C, and the reaction mixture was stirred at 0 °C for 2 h. The excess of hydride was decomposed with ethyl acetate (30 cm^3), and the resulting mixture was acidified with 10% hydrochloric acid to pH 2. The mixture was heated under reflux for 8 h, and extracted with AcOEt. The extract was washed successively with aq. sodium hydrogen carbonate and brine, and evaporated to give a pale yellow oil (8.2 g), which, on column chromatography ($CHCl_3$), gave compound **8a**[9] (4.35 g, 65%) as an oil, bp 157–160 °C/3 mmHg (Found: C, 76.0; H, 5.8%; M^+, 174.0686. $C_{11}H_{10}O_2$ requires C, 75.84; H, 5.79%; M, 174.0680); $\nu_{max}(CHCl_3)/cm^{-1}$ 1782, 1746 and 1639; δ_H 3.74 (2 H, br s), 4.70–4.73 (2 H, m), 5.81 (1 H, tt, *J* 1.8 and 1.8) and 7.15–7.40 (5 H, m); δ_C 35.2 (t), 72.7 (t), 116.6 (d), 127.4 (d), 128.6 (d), 129.0 (d), 135.5 (s), 168.9 (s) and 173.6 (s); *m*/*z* 174 (M^+, 35%), 145 (11), 115 (25), 96 (100) and 91 (38).

Preparation of 4-(α-substituted benzylidene)tetrahydrofuran-2-ones 11

4-(1-Phenylethylidene)tetrahydrofuran-2-one 11b. Following a method similar to that used for the reduction of compound **9a**, 1-ethyl 4-hydrogen 2-(1-phenylethylidene)succinate **9b** (7.0 g,

28.2 mmol) was treated with LAH (1.1 g, 28.9 mmol). After the decomposition of the excess of hydride, the resulting mixture was acidified with 10% sulfuric acid to pH 2, and heated under reflux for 1 h. The reaction mixture was extracted with AcOEt. Work-up and removal of the solvent gave a pale yellow oil (5.6 g), which, on column chromatography ($CHCl_3$), gave a product (3.8 g, 72%) as a pale yellow semi-solid. ^1H NMR spectroscopy of the product showed it to consist of a 1:1 mixture of compounds (E)- and (Z)-**11b**, mp 52–61 °C (Found: M^+, 188.0837. $C_{12}H_{12}O_2$ requires M, 188.0837); $\nu_{max}(CHCl_3)/cm^{-1}$ 1775; δ_H 1.98 (1.5 H, tt, *J* 2.0 and 2.0), 2.05 (1.5 H, tt, *J* 2.0 and 2.0), 3.19 (1 H, tq, *J* 2.0 and 2.0), 3.32 (1 H, tq, *J* 2.0 and 2.0), 4.80 (1 H, tq, *J* 2.0 and 2.0), 5.00 (1 H, tq, *J* 2.0 and 2.0) and 7.10–7.38 (5 H, m); δ_C 19.3/21.3 (q), 33.0/33.1 (t), 71.4/71.6 (t), 125.0/125.1 (s), 126.8/126.9 (d), 127.3/127.5 (d), 128.5/128.6 (d), 131.2/131.8 (s), 140.7/141.6 (s) and 175.5/175.6 (s); *m/z* 188 (M^+, 19%), 129 (30), 115 (27), 110 (100) and 105 (29).

Similarly obtained were: (E)-4-[*cyclohexyl(phenyl)methylene*]*tetrahydrofuran-2-one* **11c** {2.8 g, 69% yield from (*E*)-1-ethyl 4-hydrogen 2-[cyclohexyl(phenyl)methylene]-succinate **9c**[1] (5.0 g, 15.8 mmol)} as prisms, mp 115–116 °C (from EtOH) (Found: C, 79.7; H, 7.7%; M^+, 256.1455. $C_{17}H_{20}O_2$ requires C, 79.65; H, 7.86%; M, 256.1463); $\nu_{max}(CHCl_3)/cm^{-1}$ 1777; δ_H 0.99 (1 H, ddddd, *J* 13.0, 13.0, 13.0, 3.5 and 3.5), 1.11 (2 H, dddd, *J* 13.0, 12.5, 12.5 and 3.5), 1.27 (2 H, ddddd, *J* 13.0, 13.0, 13.0, 3.5 and 3.5), 1.57–1.68 (3 H, m), 1.69–1.76 (2 H, m), 2.22 (1 H, dddd, *J* 12.5, 12.5, 3.5 and 3.5), 2.84 (2 H, t, *J* 2.0), 5.05 (2 H, t, *J* 2.0), 6.98–7.08 (2 H, m) and 7.26–7.38 (3 H, m); δ_C 25.6 (t), 26.3 (t), 31.0 (t), 32.9 (t), 42.2 (d), 70.5 (t), 124.7 (s), 127.1 (d), 128.2 (d), 128.4 (d), 139.4 (s), 142.2 (s) and 175.6 (s); *m/z* 256 (M^+, 2%), 174 (100), 129 (42) and 115 (14); and 4-(diphenylmethylene)tetrahydrofuran-2-one **11d** [3.1 g, 77% yield from 1-ethyl 4-hydrogen 2-(diphenylmethylene)succinate **9d** (5.0 g, 16.1 mmol)] as prisms, mp 158–159 °C (from EtOH) (lit.,[30a] 159–161 °C, lit.,[30b] 150–152 °C).

Preparation of 4-(α-substituted benzyl)dihydrofuran-2-ones 8

4-(1-Phenylethyl)-2,5-dihydrofuran-2-one 8b. A mixture of compound **11b** (830 mg, 4.41 mmol), PTSA (200 mg, 1.16 mmol) and DMSO (10 cm^3) was heated at 150 °C for 9 h. The reaction mixture was poured into brine, and extracted with benzene. The extract was washed with brine, and evaporated to give a pale brown oil (900 mg), which, on column chromatography (benzene), gave *compound* **8b** (680 mg, 82%) as prisms, mp 41–42 °C (from diethyl ether) (Found: C, 76.5; H, 6.4%; M^+, 188.0835. $C_{12}H_{12}O_2$ requires C, 76.57; H, 6.43%; M, 188.0837); $\nu_{max}(CHCl_3)/cm^{-1}$ 1785, 1750 and 1633; δ_H 1.58 (3 H, d, *J* 7.5), 3.79 (1 H, br q, *J* 7.5), 4.57 (1 H, dd, *J* 17.5 and 2.0), 4.67 (1 H, dd, *J* 17.5 and 2.0), 5.92 (1 H, td, *J* 2.0 and 2.0), 7.15–7.19 (2 H, m), 7.25–7.31 (1 H, m) and 7.35–7.37 (2 H, m); δ_C 19.9 (q), 39.9 (d), 72.2 (t), 115.1 (d), 127.0 (d), 127.5 (d), 129.0 (d), 141.5 (s), 173.65 (s) and 173.72 (s); *m/z* 188 (M^+, 15%), 129 (24), 115 (24), 110 (100) and 105 (24).

Similarly prepared were: 4-[cyclohexyl(phenyl)methyl]-2,5-dihydrofuran-2-one **8c** [310 mg, 62% yield from **11c** (500 mg, 1.95 mmol)]: oil, bp 205–207 °C/2 mmHg (Found: C, 79.8; H, 7.9%; M^+, 256.1450. $C_{17}H_{20}O_2$ requires C, 79.65; H, 7.86%; M, 256.1463); $\nu_{max}(CHCl_3)/cm^{-1}$ 1784, 1748 and 1632; δ_H 0.78–0.86 (1 H, m), 0.94–1.03 (1 H, m), 1.09–1.34 (3 H, m), 1.42–1.50 (1 H, m), 1.62–1.69 (2 H, m), 1.74–1.80 (1 H, m), 1.82–1.95 (2 H, m), 3.34 (1 H, br d, *J* 10.0), 4.65 (2 H, d, *J* 2.0), 5.99 (1 H, td, *J* 2.0 and 2.0), 7.10–7.15 (2 H, m) and 7.24–7.37 (3 H, m); δ_C 25.9 (t), 26.0 (t), 26.1 (t), 31.0 (t), 32.0 (t), 40.6 (d), 53.0 (d), 72.3 (t), 115.4 (d), 127.4 (d), 128.1 (d), 128.9 (d), 139.1 (s), 171.9 (s) and 173.8 (s); *m/z* 256 (M^+, 2%), 174 (100), 129 (40) and 115 (14); and 4-*benzhydryl*-2,5-*dihydrofuran*-2-*one* **8d** [363 mg, 79% yield from **11d** (460 mg, 1.84 mmol)]: needles, mp 75.5–76 °C (from cyclohexane) (Found: C, 81.5; H, 5.7%; M^+, 250.0969. $C_{17}H_{14}O_2$ requires C, 81.58; H, 5.64%; M, 250.0994); $\nu_{max}(CHCl_3)/cm^{-1}$ 1783, 1751 and 1633; δ_H 4.75 (2 H, d, *J* 2.0), 5.05 (1 H, br s), 5.71 (1 H, td, *J* 2.0 and 2.0), 7.15–7.20 (4 H, m) and 7.27–7.38 (6 H, m); δ_C 51.5 (d), 72.7 (t), 118.6 (d), 127.6 (d), 128.4 (d), 129.0 (d), 139.4 (s), 171.7 (s) and 173.3 (s); *m/z* 250 (M^+, 96%), 205 (67), 191 (42), 172 (100), 165 (53) and 115 (63).

Cycloaddition of diazomethane with 2-phenylmaleic anhydride 14

An ethereal solution of diazomethane was added to a stirred suspension of compound **14**[10] (2.0 g, 11.5 mmol) in diethyl ether (20 cm^3). Soon after the suspension had become a clear solution, the formation of precipitates was observed. The precipitates were filtered off, and the collected solid was washed with diethyl ether to give the 1-pyrazoline **15** (1.96 g, 79%) as a powder, mp 70–71 °C (decomp.); δ_H 3.73 (1 H, dd, *J* 9.5 and 2.0), 5.10 (1 H, dd, *J* 18.5 and 9.5), 5.44 (1 H, dd, *J* 18.5 and 2.0) and 7.44–7.49 (5 H, m). Gradual decomposition of compound **15** into anhydrides **16** and **17** accompanied by the evolution of nitrogen was observed in $CDCl_3$ at room temperature.

Pyrolysis of the 1-pyrazoline 15

A solution of compound **15** (1.96 g, 9.1 mmol) in benzene (50 cm^3) was heated at 70 °C until evolution of nitrogen had ceased. Removal of the solvent gave a crude product (1.9 g) as an oil, which was used in the next step without purification. ^1H NMR spectroscopy of the oil showed it to consist of a 3:1 mixture of 1-phenyl-3-oxabicyclo[3.1.0]hexane-2,4-dione **16**[12] and 2-methyl-3-phenylmaleic anhydride **17**,[13] respectively.

A mixture of anhydrides **16** and **17**: δ_H 2.00 (0.75 H, dd, *J* 8.5 and 5.0), 2.09 (0.75 H, dd, *J* 5.0 and 3.5), 2.32 (0.75 H, s), 2.99 (0.75 H, dd, *J* 8.5 and 3.5) and 7.28–7.78 (5 H, m); δ_C 10.7 (q), 24.1 (t), 27.4 (d), 37.3 (s), 128.2 (s), 128.7 (d), 128.9 (d), 129.0 (d), 129.1 (d), 129.3 (d), 129.6 (s), 130.9 (d), 138.7 (s), 139.8 (s), 164.8 (s), 166.1 (s), 167.2 (s) and 168.6 (s). The two anhydrides were separated by GC-MS; for the major anhydride **16** (Found: M^+, 188.0454. $C_{11}H_8O_3$ requires M, 188.0474); *m/z* 188 (M^+, 37%), 144 (36) and 115 (100). For the minor anhydride **17** (Found: M^+, 188.0501); *m/z* 188 (M^+, 64%) and 116 (100).

Sodium boranuide reduction of anhydrides 16 and 17

A solution of anhydrides **16** and **17** (1.9 g) in THF (20 cm^3) was added to a stirred suspension of sodium boranuide (600 mg, 15.8 mmol) in THF (10 cm^3) at 0 °C, and the resulting mixture was stirred at 0 °C for 1 h. After addition of water (10 cm^3), the mixture was acidified with 10% hydrochloric acid to pH 2. The resulting mixture was stirred at room temperature for 5 h, and extracted with diethyl ether. The extract was washed with brine, and evaporated to give an oil (1.75 g), which, on column chromatography [hexane–diethyl ether (5:1)], gave 1-phenyl-3-oxabicyclo[3.1.0]hexan-2-one **7a** (584 mg, 37%), 5-phenyl-3-oxabicyclo[3.1.0]hexan-2-one **12a** (284 mg, 18%), 4-methyl-3-phenyl-2,5-dihydrofuran-2-one **18** (157 mg, 10%), and 3-methyl-4-phenyl-2,5-dihydrofuran-2-one **19** (110 mg, 7%).

1-Phenylbicyclic lactone **7a**: prisms, mp 23–25 °C (from diethyl ether) (lit.,[14a] 49–50 °C); bp 115–116 °C/0.01 mmHg (lit.,[14a] 119 °C/0.1 mmHg) (Found: M^+, 174.0659. $C_{11}H_{10}O_2$ requires M, 174.0681); $\nu_{max}(CHCl_3)/cm^{-1}$ 1765; δ_H 1.37 (1 H, dd, *J* 4.8 and 4.8), 1.65 (1 H, dd, *J* 7.6 and 4.8), 2.56 (1 H, ddd, *J* 7.6, 4.8 and 4.8), 4.29 (1 H, d, *J* 9.5), 4.46 (1 H, dd, *J* 9.5 and 4.8) and 7.25–7.46 (5 H, m); δ_C 20.1 (t), 25.1 (d), 31.7 (s), 68.0 (t), 127.7 (d), 128.3 (d), 128.6 (d), 134.1 (s) and 175.9 (s); *m/z* 174 (M^+, 100%), 144 (55), 129 (41) and 115 (90).

5-Phenylbicyclic lactone **12a**: waxy solid, mp 28–29 °C; bp 125–127 °C/0.001 mmHg (Found: M^+, 174.0659); $\nu_{max}(CHCl_3)/cm^{-1}$ 1768; δ_H 1.38 (1 H, dd, *J* 4.8 and 3.5), 1.70 (1 H, dd, *J* 9.3 and 4.8), 2.32 (1 H, dd, *J* 9.3 and 3.5), 4.47 (1 H, d, *J* 9.0),

4.50 (1 H, *J* 9.0) and 7.24–7.42 (5 H, m); δ_C 19.0 (t), 24.6 (d), 33.6 (s), 73.4 (t), 127.8 (d), 127.9 (d), 128.8 (d), 136.5 (s) and 175.6 (s); *m/z* 174 (M^+, 56%), 145 (50), 129 (53), 115 (100) and 91 (28).

The 4-methylbutenolide **18**: needles, mp 83–84 °C (from diisopropyl ether) (lit.,[15a] 84–86 °C; lit.,[15b] 84.5–86 °C).

The 3-methylbutenolide **19**: needles, mp 122.5–123 °C (from diisopropyl ether) (lit.,[16a] 121–122 °C; lit.,[16b] 115–117 °C; lit.,[16c] 120–122 °C).

Catalytic hydrogenation of compound 8a

A suspension of 5% palladium on carbon (50 mg) in ethanol (5 cm^3) was pre-equilibrated with hydrogen. A solution of compound **8a** (100 mg, 0.57 mmol) in ethanol (5 cm^3) was added, and the mixture was hydrogenated at room temp. and atmospheric pressure until the uptake of hydrogen ceased. The catalyst was filtered off, and the filtrate was evaporated to give an oil (101 mg), which, on distillation at reduced pressure, gave 4-benzyltetrahydrofuran-2-one **20** (100 mg, 99%) as an oil, bp 158–160 °C (5 mmHg) [lit.,[17b] 162–163 °C (6 mmHg)].

Photolysis of 4-(α-substituted benzyl)-2,5-dihydrofuran-2-ones 8

General procedure. In the presence of 1,4-diazabicyclo-[2.2.2]octane§ (DABCO) (40 mg, 0.35 mmol) a solution of compound **8** (100 mg) was irradiated in methanol (200 cm^3) or acetone (200 cm^3) (time and product distribution are given in Table 1). Products were isolated by column chromatography of the residue obtained after removal of the solvent. Column chromatography of the residue from compound **8a** was carried out by using hexane–diethyl ether (1:1) as eluent. Solvent system used for elution of the residue from substrates **8b–8d** was hexane–acetone (20:1).

Photolysis of compound 8a in methanol. A cyclopropano lactone **12a**, a photoreduced product **20**, 4-*benzyl*-4-(*hydroxymethyl*)*tetrahydrofuran*-2-*one* **21** and *methyl* trans-2-(*hydroxymethyl*)-2-*phenylcyclopropane*-1-*carboxylate* **23** were obtained from compound **8a**, and formation of 4-*benzyl*-3-(*hydroxymethyl*)*tetrahydrofuran*-2-*one* **22** was detected by GC-MS analysis. A small amount of the starting material was also recovered. Compound **12a** was identical with the authentic specimen synthesized *via* the alternative route, and compound **20** with the compound obtained by the hydrogenation of compound **8a**, respectively.

The 4-(*hydroxymethyl*)*tetrahydrofuranone* **21**: oil, bp 135–137 °C/0.02 mmHg (Found: M^+, 206.0916. $C_{12}H_{14}O_3$ requires M, 206.0943); $\nu_{max}(CHCl_3)/cm^{-1}$ 3450 and 1771; δ_H 1.81 (1 H, br s, exchangeable with D_2O), 2.42 (1 H, d, *J* 17.5), 2.48 (1 H, d, *J* 17.5), 2.83 (1 H, d, *J* 13.0), 2.90 (1 H, d, *J* 13.0), 3.54 (2 H, br s-like), 4.16 (1 H, d, *J* 9.0), 4.22 (1 H, d, *J* 9.0) 7.13–7.18 (2 H, m) and 7.23–7.41 (3 H, m); δ_C 36.3 (t), 39.7 (t), 45.6 (s), 64.8 (t), 73.9 (t), 127.1 (d), 128.6 (d), 130.0 (d), 136.1 (s) and 176.7 (s); *m/z* 206 (M^+, 17%), 188 (5), 129 (11), 115 (16) and 91 (100).

The methyl cyclopropano ester **23**: oil, bp 98–100 °C/0.008 mmHg (Found: M^+, 206.0925); $\nu_{max}(CHCl_3)/cm^{-1}$ 3430 and 1722; δ_H 1.36 (1 H, dd, *J* 8.0 and 5.0), 1.64 (1 H, br s, exchangeable with D_2O), 1.74 (1 H, dd, *J* 5.5 and 5.0), 2.10 (1 H, dd, *J* 8.0 and 5.5), 3.43 (3 H, s), 3.57 (1 H, d, *J* 11.0), 3.80 (1 H, d, *J* 11.0) and 7.18–7.42 (5 H, m); δ_C 16.1 (t), 24.5 (d), 37.8 (s), 51.6 (q), 70.0 (t), 127.5 (d), 128.5 (d), 129.8 (d), 137.8 (s) and 171.3 (s); *m/z* 206 (M^+, 5%), 174 (67), 188 (7), 129 (53), 120 (100), 115 (60) and 91 (66).

The 3-(*hydroxymethyl*)*tetrahydrofuranone* **22** (Found: M^+, 206.0914); *m/z* 206 (M^+, 4%), 142 (35), 129 (12), 117 (39) and 91 (100).

Photolysis of compound 8b in methanol. A 10:1 mixture (by ^1H NMR spectroscopy) of endo-6-*methyl*-5-*phenyl*-3-*oxabicyclo*[3.1.0]*hexan*-2-*one* endo-**12b** and its exo-*isomer* exo-**12b** was obtained from substrate **8b**.

A *mixture of* endo- *and* exo-*bicyclic lactone* endo- *and* exo-**12b** (Found: M^+, 188.0829. $C_{12}H_{12}O_2$ requires M, 188.0837); δ_H 1.01 (0.27 H, t, *J* 6.5), 1.30 (2.73 H, d, *J* 6.5), 1.64 (0.09 H, qd, *J* 6.5 and 3.0), 1.89 (0.91 H, dq, *J* 9.0 and 6.5), 2.12 (0.09 H, dd, *J* 3.0 and 0.8), 2.45 (0.91 H, dd, *J* 9.0 and 1.0), 4.25 (0.09 H, d, *J* 9.0), 4.46 (0.91 H, br d, *J* 10.0), 4.49 (0.09 H, dd, *J* 9.0 and 0.8), 4.52 (0.91 H, d, *J* 10.0) and 7.18–7.40 (5 H, m); δ_C(minor isomer/major isomer) 8.0/8.1 (q), 26.4/23.8 (d), 29.7/29.9 (d), 38.7/38.0 (s), 74.3/70.0 (t), 127.5 (d), 128.0/127.8 (d), 129.0/128.9 (d), 134.2/138.1 (s) and 175.6/174.2 (s); *m/z* 188 (M^+, 22%), 144 (44), 129 (100), 115 (26) and 91 (18).

Photolysis of compound 8c in methanol. endo-6-*Cyclohexyl*-5-*phenyl*-3-*oxabicyclo*[3.1.0]*hexan*-2-*one* endo-**12c** and its exo-*isomer* exo-**12c** were obtained from substrate **8c**.

endo-*Bicyclic lactone* endo-**12c**: prisms, mp 53–54 °C (from hexane) (Found: C, 79.6; H, 7.9%; M^+, 256.1462. $C_{17}H_{20}O_2$ requires C, 79.65; H, 7.86%; M, 256.1463); $\nu_{max}(CHCl_3)/cm^{-1}$ 1763; δ_H 1.16–1.40 (6 H, m), 1.59 (1 H, dd, *J* 9.5 and 9.5), 1.66–1.95 (5 H, m), 2.42 (1 H, dd, *J* 9.5 and 1.0), 4.41 (1 H, br d, *J* 10.0), 4.47 (1 H, d, *J* 10.0) and 7.20–7.37 (5 H, m); δ_C 25.7 (t), 25.8 (t), 26.1 (t), 29.2 (d), 32.5 (t), 32.6 (d), 33.2 (t), 35.6 (d), 38.6 (s), 70.8 (t), 127.8 (d), 128.0 (d), 128.9 (d), 138.3 (s) and 174.5 (s); *m/z* 256 (M^+, 2%), 174 (29), 161, (100), 129 (19) and 91 (11).

exo-*Bicyclic lactone* exo-**12c**: prisms, mp 156–158 °C (from light petroleum) (Found: C, 79.6; H, 7.85%; M^+, 256.1462); $\nu_{max}(CHCl_3)/cm^{-1}$ 1772 and 1758; δ_H 0.66 (1 H, ddddd, *J* 10.5, 10.5, 10.5, 3.5 and 3.5), 0.80–0.90 (1 H, m), 0.98–1.28 (4 H, m), 1.35 (1 H, dd, *J* 10.5 and 3.5), 1.49–1.80 (5 H, m), 2.28 (1 H, dd, *J* 3.5 and 1.0), 4.26 (1 H, d, *J* 9.0), 4.57 (1 H, dd, *J* 9.0 and 1.0) and 7.15–7.25 (5 H, m); δ_C 25.6 (t), 25.7 (t), 26.0 (t), 26.6 (d), 32.1 (t), 32.5 (t), 36.3 (d), 38.2 (s), 39.1 (d), 74.2 (t), 127.9 (d), 128.2 (d), 128.7 (d), 134.7 (s) and 175.6 (s); *m/z* 256 (M^+, 2%), 174 (13), 161 (100), 129 (13) and 91 (10).

Photolysis of compound 8d in methanol. endo-5,6-*Diphenyl*-3-*oxabicyclo*[3.1.0]*hexan*-2-*one* endo-**12d** and its *exo*-isomer *exo*-**12d** were obtained from substrate **8d**.

endo-*Bicyclic lactone* endo-**12d**: prisms (lit.,[32] oil), mp 90–92 °C (from hexane–acetone).

exo-Bicyclic lactone *exo*-**12d**: prisms, mp 126.5–127.5 °C (from hexane) (lit.,[32] 124–125 °C).

Photolysis of compound 8a in acetone. The cyclopropano lactone **12a**, 4-benzyl-3-(2-hydroxypropan-2-yl)tetrahydrofuran-2-one **24** and the photoreduced product **20** were obtained from substrate **8a**. A small amount of the starting material was also recovered. Compound **12a** was identical with the authentic specimen synthesized *via* the alternative route, and compound **20** with the authentic sample obtained by hydrogenation of compound **8a**.

The (2-*hydroxypropan*-2-*yl*)*tetrahydrofuranone* **24**: prisms, mp 106–107 °C (from hexane–diethyl ether) (Found: C, 71.9; H, 7.85. $C_{14}H_{18}O_3$ requires C, 71.77; H, 7.74%); $\nu_{max}(CHCl_3)/cm^{-1}$ 3450 and 1762; δ_H 0.86 (3 H, s), 1.27 (3 H, s), 1.44 (1 H, br s, exchangeable with D_2O), 2.52–2.62 (1 H, m), 2.72–2.82 (3 H, m), 3.76 (2 H, br s) and 7.25–7.40 (5 H, m); δ_C 21.7 (q), 28.2 (q), 34.3 (t), 47.5 (d), 48.9 (d), 66.3 (t), 87.4 (s), 127.5 (d), 128.5 (d), 128.8 (d), 140.0 (s) and 175.0 (s); *m/z* 219 ($M^+ - 15$, 1%), 204 (33), 145 (25), 117 (100) and 91 (25).

Photolysis of compound 8b in acetone. Bicycle *endo*-**12b**, contaminated with a trace amount of its diastereoisomer *exo*-**12b** (by ^1H NMR spectroscopy), was obtained from substrate **8b**.

§ Although oxygen in the nitrogen gas was supposed to have been washed out by passage of the gas through an alkaline pyrogallol solution, DABCO was added in order to avoid the influence of singlet oxygen (*cf.* ref. 31) which might be generated from any remaining oxygen.

Photolysis of compound 8c in acetone. Bicycle *endo*-**12c** and its diastereoisomer *exo*-**12c** were obtained from substrate **8c**.

Photolysis of compound 8d in acetone. Bicycle *endo*-**12d** and its diastereoisomer *exo*-**12d** were obtained from substrate **8d**.

Photolysis of compound 12a in methanol

A mixture of compound **12a** (42 mg, 0.24 mmol), DABCO (16 mg, 0.14 mmol) and methanol (80 cm^3) was irradiated for 23 h to give a pale yellow oil (65 mg), which, on column chromatography [hexane–diethyl ether (1 : 1)], gave compound **23** (4.6 mg, 9%) and the starting material **12a** (7 mg, 17% recovery).

Attempted acidic methanolysis of compound 12a

A mixture of compound **12a** (7.5 mg, 0.04 mmol), PTSA (5 mg, 0.03 mmol) and methanol (2 cm^3) was heated under reflux for 5 h. The reaction mixture was poured into aq. sodium hydrogen carbonate (10 cm^3), and extracted with chloroform. Removal of the solvent resulted in the complete recovery of the starting material.

Photoisomerization of bicycle *exo*-12d

Under argon, a mixture of bicycle *exo*-**12d** (10 mg, 0.04 mmol) and degassed acetone (1 cm^3) in a Pyrex test tube was irradiated for 5 h. Removal of the solvent left an oil (10 mg) which was a 2.8 : 1 diastereoisomeric mixture of bicycles *exo*-**12d** and *endo*-**12d**, respectively (by ^1H NMR spectroscopy).

Photoisomerization of compound *endo*-12d

Compound *endo*-**12d** (10 mg, 0.04 mmol) was irradiated for 5 h under the same conditions as those described for the photoirradiation of its diastereoisomer *exo*-**12d**, to give an oil, which was a 1 : 3.4 mixture of *exo*-**12d** and *endo*-**12d**, respectively (by ^1H NMR spectroscopy).

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