Furan-2(3*H*)- and 2(5*H*)-ones. Part 5.[1] Photoreactions of 3-Benzylfuran-2(5*H*)-ones; Cyclisation to Indenofuranones[2]

Osamu Muraoka,*[,a] Genzoh Tanabe,[a] Kyohko Sano,[a] Toshie Minematsu,[a] and Takefumi Momose*[,b]

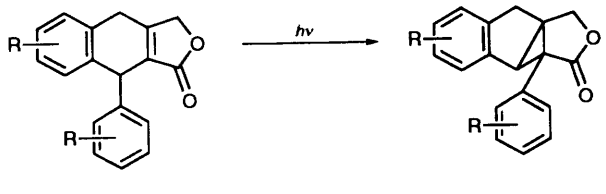
[a] *Faculty of Pharmaceutical Sciences, Kinki University, Kowakae 3-4-1, Higashi-Osaka, Osaka 577, Japan*

[b] *Faculty of Pharmaceutical Sciences, Toyama Medical and Pharmaceutical University, Sugitani 2630, Toyama 930-01, Japan*

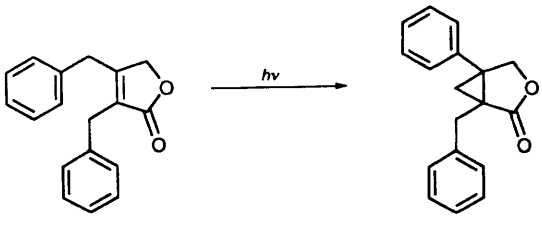
The effect of substitution at the 'central methane' on the photoreactivity of 3-benzylfuran-2(5*H*)-ones **5a–g** was investigated. Despite its di-π-methane structure, photochemical arylation was effected to give substituted indenofuranones **6** in good yields. Only the substitution by phenyl caused the di-π-methane rearrangement to give a cyclopropanofuranone **18g** in moderate yield.

The di-π-methane rearrangement has proved to be one of the most ubiquitous of photochemical rearrangements, and most typically involves the conversion of a molecule having a di-π-methane moiety, *i.e.* having two π systems bound to a single sp^3 carbon, into a cyclopropane appended with a π substituent.[3] An interesting fact in the di-π-methane rearrangement of β-apolignans **1** is the observation that the regiospecific rearrangement of species **1** into tetrahydrocyclopropa[*a*]indenes **2** is common irrespectively of their ring substituents, and that only the pendant phenyl (the phenyl at the α- and not the β-butenolidylmethyl system) migrates among the three possible di-π-methane systems found in the β-apolignans.[4]

In a previous paper dealing with the selectivity in migration in systems **1**, we examined the photoreactivity of 3,4-dibenzylfuran-2(5*H*)-one **3**, a system lacking the stereochemical rigidity of compounds **1**, and found that only the β-butenolide system migrated to give a cyclopropane **4**.[1] No rearrangement of the 3-benzyl moiety was detected, in contrast with the case of β-apolignans **1**.

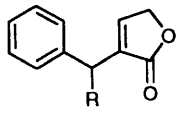


1 **2**



3 **4**

In order to inquire into the origin of the selectivity found for compounds **1**, we examined the photoreactivity of the 3-(α-substituted benzyl)furan-2(5*H*)-one system **5** from the viewpoint of examining the spatial factors in the substituted 'central methane' carbon, because Zimmerman *et al.* had reported the acceleration of the di-π-methane rearrangement by the introduction of substituents on the 'central methane' carbon in the photoirradiation of the divinylmethane system.[5] Despite its di-π-methane structure, introduction of appropriate substituents on the 'central methane' resulted in characteristic photoarylation, affording functionalised tetrahydroindenofuranones **6** in good yields.



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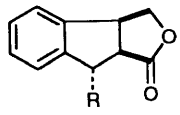

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Results

Synthesis of 3-(α-*Substituted Benzyl*)*furan*-2(5H)-*ones* **5a–g**.—A general procedure starting with 3-benzyltetrahydrofuran-2-ones **7** *via* sulfenylation/oxidation/elimination by Trost's protocol[6] worked well with the α-substituted benzyl system **7b–g**. However, it was found to be unsuccessful with the α-non-substituted system **7a**, and thus the preparation of 3-benzylfuran-2(5*H*)-one **5a** was attempted by two other procedures.†

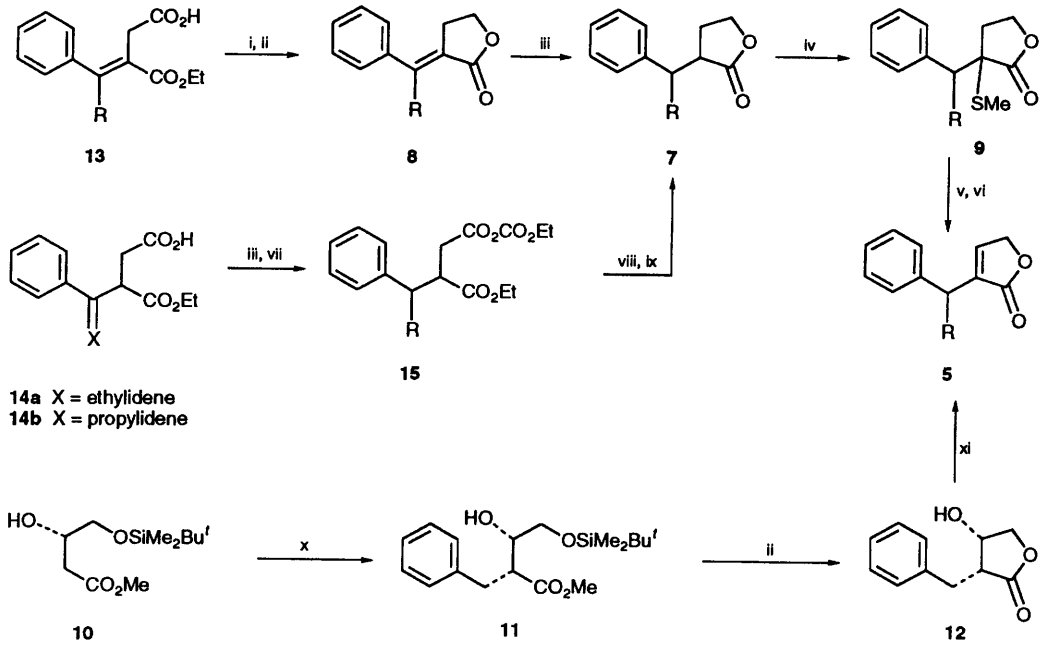
Hydrogenation of α-benzylidenebutyrolactone **8a**[8] and subsequent sulfenylation of the resulting 3-benzyltetrahydrofuran-2-one **7a**,[8a,9] according to Trost's method,[6] gave 3-benzyl-3-(methylsulfanyl)tetrahydrofuran-2-one **9a** in 58% yield (Scheme 1). The sodium metaperiodate oxidation of **9a** in aq. tetrahydrofuran (THF) at 50 °C followed by heating of the resulting sulfoxide in boiling toluene gave a 1:1 mixture of the desired furan-2(5*H*)-one **5a** and its regioisomer **8a** in 78% combined yield. They proved to be difficult to separate, so an alterative route was examined.

α-Alkylation, with benzyl bromide, of the dianion derived from a β-hydroxy ester, methyl (*S*)-4-[(1,1-dimethylethyl)-dimethylsiloxy]-3-hydroxybutanoate **10**,‡ proceeded in a highly stereoselective manner§ to give practically a single diastereoisomer, methyl (2*R*,3*S*)-2-benzyl-4-(*tert*-butyl-dimethylsiloxy)-3-hydroxybutanoate **11**, in 43% yield. Lactonisation of silyl ester **11** with 10% hydrochloric acid in 1,2-dimethoxyethane (DME) at 80 °C gave *cis*-3-benzyl-4-

† Several methods are known for the preparation of the furanone **5a**.[7] However, we synthesised compound **5a** *via* an independent route in the present work.

‡ Derived from dimethyl (S)-(−)-malate using BH_3·SMe_2–$NaBH_4$ (*cf.* ref. 10*a*) followed by monoprotection of the primary hydroxy group (ref. 10*b*,*c*).

§ The stereoselectivity in the alkylation of a β-hydroxy ester has been discussed (ref. 11).



Scheme 1 *Reagents and conditions:* i, BMS; ii, 10% HCl; iii, H_2, Pd–C; iv, MeSSMe, LiPr^i cyclohexyl amide; v, $NaIO_4$; vi, heat; vii, $ClCO_2Et$, NEt_3; viii, $NaBH_4$; ix, 10% H_2SO_4; x, BnBr, LDA; xi, $POCl_3$, Py

hydroxytetrahydrofuran-2-one **12**,* which was treated with phosphorus trichloride oxide in pyridine[12] to give the desired furanone **5a** in 81% overall yield from compound **11**.

The furanone **5a** displayed IR absorptions for the enone system at 1756 and 1660 cm^{-1}. The ^{1}H NMR spectrum displayed a one-proton triplet of triplets, at δ_H 6.93, due to the olefinic proton of the butenolide system. Furthermore, the ^{13}C NMR spectrum displayed resonances, at δ_C 134.1 and δ_C 145.5, due to two olefinic carbons of the butenolide moiety.

Of the 'central methane'-substituted analogues **5b–g**, four (**5b**, **5e**, **5f** and **5g**) were prepared in the following manner. Selective reduction of the carboxy group in 1-ethyl 4-hydrogen 2-alkylidenesuccinates **13b**,[13a] **13e**,[13b] **13f**[13c] and **13g**[13a] with borane–dimethyl sulfide complex (BMS) followed by acid-catalysed lactonisation of the resulting hydroxy esters afforded 3-alkylidenetetrahydrofuran-2-ones **8b**,[8b,8c] **8e**, **8f** and **8g**,[8c,14] which were subjected to catalytic hydrogenation over palladium on carbon in glacial acetic acid to give the 3-alkyltetrahydrofuran-2-ones **7b**, **7e**, **7f** and **7g**, respectively. Sulfenylation of the furanones, followed by oxidative elimination of the sulfenyl group in the resulting sulfides **9**, in the same manner as described above, afforded the desired furan-2(5*H*)-ones **5b**, **5e**, **5f** and **5g** in 53–68% overall yields from the corresponding precursor **7**. The selective formation of compounds **5** comes about as a result of the alkyl substitution at the 'central methane', which causes an *anti* relationship between the α-methylsulfanyl moiety and the adjacent benzyl methine proton; hence *syn* elimination of the sulfoxide afforded furan-2(5*H*)-ones **5** effectively.

The furanone with an ethyl or propyl appendage, compound **5c** or **5d**, was prepared starting from 1-ethyl 4-hydrogen 2-(1-phenylalk-1-enyl)succinate **14a** or **14b**.† The mixed anhydride **15** obtained by hydrogenation of compound **14** and subsequent treatment with ethyl chloroformate was reduced by sodium borohydride and subsequently subjected to acid-catalysed lactonisation of the reduction product to give compound **7c** or **7d**, which was elaborated to the corresponding butenolide **5** by the sequence described for compounds **7b–g**.

The ^{1}H NMR spectra of these furanones **5b**, **5e**, **5f** and **5g** showed one-proton signals, at δ_H 6.96–7.25, due to the olefinic proton of the butenolide system. The one-proton signal centred at δ_H 3.88, δ_H 3.59, δ_H 3.70, δ_H 3.45, δ_H 3.38 or δ_H 5.19 was responsible for the methine proton on the 'central methane' carbon in compound **5b**, **5c**, **5d**, **5e**, **5f** or **5g**, respectively.

Photoirradiation of 3-(α-*Substituted benzyl*)*furan*-2(5H)-*ones*.—Photoirradiation of 3-benzylfuran-2(5*H*)-one **5a** in methanol through a Pyrex filter gave mainly a photoreduced product **7a**‡ and a methanol adduct **16a**§ each in 20% yield. Formation of small amounts of photocyclisation product, 3,3a,8,8a-tetrahydro-1*H*-indeno[1,2-*c*]furan-1-one **6a**,¶ and another methanol adduct **17**‡ in 8 and 4% yield, respectively, was detected. No evidence for the formation of a cyclopropanolactone **18a** was detected in spite of careful examination of the products. Irradiation of compound **5a** in acetone under the same conditions as the run in methanol gave no trace amounts of tricycle **6a** but gave compound **7a** and an acetone adduct, 3-benzyl-4-(2-hydroxypropan-2-yl)tetrahydrofuran-2-one **19a**, in 17 and 53% yield, respectively. The spectral properties of compound **7a** were identical with those of the authentic specimen obtained by catalytic hydrogenation of compound **8**. The IR spectrum of *trans* adduct **16a** showed absorptions due to the hydroxy group and the lactone carbonyl at 3474 and 1764 cm^{-1}, respectively. Its ^{1}H NMR spectrum

* The *cis* stereochemistry for compound **12** was determined on the basis of the NOE enhancement between the α and β protons on the lactone ring.

† Compounds **14a** and **14b** were prepared in a manner similar to that for the preparation of compound **13**. Predominant formation of compound **14a** *via* the Stobbe condensation of diethyl succinate with propiophenone has been reported (ref. 15).

‡ Reduction or α-addition of the solvent on irradiation of an α,β-unsaturated ester in methanol has been described (ref. 16).

§ Photochemical conjugate addition of methanol to α-enones has been reported (ref. 17).

¶ Compound **6a** has appeared in the literature, but without spectral data (ref. 18).

displayed signals, at δ 2.77 and at δ 2.47, due to the methine protons on the α- and β-carbon of the lactone ring, respectively, and a pair of one-proton doublets of doublets due to the hydroxymethylene protons at δ 3.37 and δ 3.47. Moreover, compound **16a** displayed a peak due to the molecular ion at *m/z* 206 (48%) in the MS spectrum. The relative stereochemistry at Cα and Cβ on the lactone ring in compound **16a** was determined as depicted on the basis of differential nuclear Overhauser effect (NOE) experiments. A marked NOE was detected between one of the benzylic methylene protons and the methine proton on the carbon β to the lactone carbonyl, but not between the two methine protons on the lactone ring.

The ^{1}H NMR spectrum of compound **19a** displayed a pair of three-proton singlets at δ 1.07 and δ 1.15, due to two methyl groups attached to the sp^3 carbon bearing a hydroxy group, instead of the signals (δ 3.37 and δ 3.47) due to the hydroxymethylene protons in compound **16a**. Moreover, compound **19a** displayed a peak due to the molecular ion at *m/z* 234 (27%) in the MS spectrum.

The IR spectrum of compound **6a** showed an absorption due to its lactone carbonyl at 1768 cm^{-1} and no olefinic bands. Its ^{1}H NMR spectrum displayed a broad triplet-like signal, at δ 4.08, due to a methine proton on the carbon β to the carbonyl, a pair of one-proton doublet of doublets, at δ_H 4.52 and δ_H 4.67, due to the lactonic γ-methylene moiety, and signals, between δ_H 7.22 and δ_H 7.35, corresponding to four aromatic protons. Its ^{13}C NMR spectrum displayed resonances due to two substituted aromatic carbons at δ_C 141.6 and δ_C 141.9. The MS spectrum displayed a peak due to the molecular ion at *m/z* 174 (55%).

Photoirradiation of the 'central methane'-substituted systems **5b–f** in methanol through a Pyrex filter afforded mainly the corresponding photocyclisation products **6b–f** with concomitant formation of the photoreduced products **7b–f** and methanol adducts **16b–f**, respectively. Additionally, a product possessing a cyclobutane structure **20*** was obtained as one of the minor products on irradiation of compound **5e**. The product distributions are shown in Table 1.

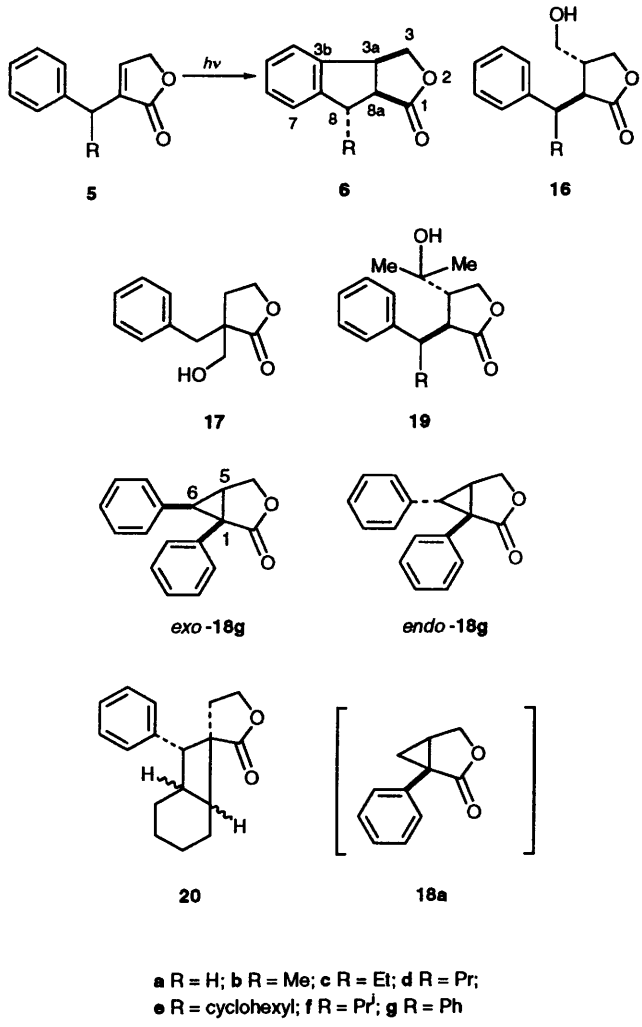
The spectral properties of photocyclisation products **6b–f** were similar, and are suggestive of a tetrahydroindenofuranone structure of the same type as **6a**. The stereochemistry of compound **6e** was assigned on the basis of differential NOE experiments. A marked NOE was detected between the α- and β-proton on the lactone ring, but not between the α-ketonic proton and the benzylic methine proton.

Only the butenolide **5g** led, upon irradiation in methanol, to formation of a moderate amount of the products of the di-π-methane rearrangement, *viz. exo*- and *endo*-1,6-diphenyl-3-oxabicyclo[3.1.0]hexan-2-one (*exo*-**18g** and *endo*-**18g**), along with a photocyclised product **6g**. When compound **5g** was irradiated under the acetone-photosensitised conditions, the efficiency of the di-π-methane rearrangement was increased, and compounds **18g** were obtained in 64% combined yield.

The product **18g** showed photointerconversion between *exo* and *endo* isomers in acetone-photosensitised irradiation. The formation of two diastereoisomeric isomers *exo*- and *endo*-**18g** is attributed to readily occurring photoisomerisation in the bicyclo[3.1.0]hexane system.[20]

The major cyclopropanolactone *exo*-**18g** resulting from compound **5g** showed an IR absorption due to the lactone carbonyl at 1768 cm^{-1}, and a peak due to the molecular ion at *m/z* 250 (31%) in the MS spectrum. Its ^{1}H NMR spectrum displayed a one-proton doublet, at δ 2.71, due to a methine proton on C-6. Both the one-proton doublet at δ 4.50 and the one-proton doublet of doublets at δ 4.62 corresponded to the lactonic γ-methylene moiety. A significant downfield shift of the signal at δ 3.09 due to the methine proton on C-5 is ascribed to the deshielding effect of the phenyl on C-6, indicating that the phenyl ring is of *exo* orientation. Furthermore, the *exo*-oriented phenyl ring at C-6 caused the signals due to two aromatic protons at the *ortho* position in the phenyl on C-1 to shift upfield to δ 6.82–6.86. The observed small vicinal coupling ($J_{5,6}$ 4.5 Hz)† between the two cyclopropane protons on C-5 and C-6 suggested their *trans* relationship, supporting the assigned stereochemistry. Further support was given by the differential NOE experiments. A marked NOE enhancement appeared between one of the lactonic γ-methylene protons and the methine proton on C-6, but not between the two methine protons on the cyclopropane ring.

The minor isomer *endo*-**18g** showed similar behaviour in its



a R = H; **b** R = Me; **c** R = Et; **d** R = Pr; **e** R = cyclohexyl; **f** R = Pr^i; **g** R = Ph

* Hydrogen abstraction by the β-carbon of an enone system to give a spiro compound has been described (ref. 19). A singlet at δ_C 53.8 and three doublets at δ_C 42.9, 46.1 and 52.9 in the off-resonance ^{13}C NMR spectrum of compound **20** are evidence for the characteristic spiro-structure of compound **20**. The relative stereochemistry of compound **20** is evident on the basis of a significant downfield shift, resulting from the deshielding effect of the lactone carbonyl, of a signal, at δ_H 3.70, due to the benzylic methine proton. No NOE was detected between this and the lactonic β-methylene protons. However, concerning the relative stereochemistry at the other two chiral centres on the cyclobutane, we could not establish the α or β orientation of two kinds of methine protons on C-1 and C-6, resonating at δ_H 1.95 and 2.08, respectively, from its NOESY spectrum or its differential NOE experiment in the present study.

† The one with a large coupling constant was usually found to correspond to the *endo*-isomer (ref. 21).

Table 1a[a]

Substrate		Reaction	Products (isolated yield %)						
5	R	time (t/h)	**6**	*endo*-**18**	*exo*-**18**	**16**	**7**	**17**	**20**
a	H	23	8			20	20	4	
b	Me	19	42			10	4		
c	Et	19	50			10	3		
d	Pr	19	64			10	3		
e	Cyclohexyl	5	78			trace	2		1.5
f	Pr^i	14	80			7	2		
g	Ph	14	58	6	23	3	trace		

[a] Results in methanol.

Table 1b[b]

Substrate		Reaction	Products (isolated yield %)				
5	R	time (t/h)	*endo*-**18**	*exo*-**18**	**19**	**7**	**20**
a	H	6			53	17	
b	Me	11			14	12	
e	Cyclohexyl	11			19	9	11
g	Ph	6	17	47	15	trace	

[b] Results in acetone.

IR (C=O at 1764 cm^{-1}) and MS [*m*/*z* 250 (41%)] spectroscopic properties. The *endo*-oriented phenyl ring was evidenced both by an upfield shift of the signal at δ 4.18 due to one of the lactonic γ-methylene protons, possibly by the shielding effect of the phenyl ring, and by a downfield shift of the signal at δ 3.10 due to the methine proton on C-6, as compared with that of compound *exo*-**18** (δ 2.71), owing to the anisotropy of the phenyl ring on C-1. Moreover, the vicinal protons on the cyclopropane exhibited a large coupling constant ($J_{5,6}$ 8.5 Hz). In the differential NOE experiments, irradiation of the signal at δ 3.10 due to the *exo*-proton on C-6 enhanced the integrals of both aromatic protons at the *ortho* positions in the phenyl group at position 1. An additional NOE enhancement appeared between the aromatic protons at C-6 and one of the lactonic γ-methylene protons.

Discussion

The predominant photochemical arylation encountered in the irradiation of compounds **5** is attributable to readily occurring radical formation at the β position in the enone system. Carbonyl compounds can be expected to acquire an intensified basicity in the triplet excited state and to abstract a proton from a protic solvent, and an increase in the positive charge on the β-position can also be expected.[22] Thus, the β-carbon of compounds **5** must become more electrophilic by excitation to attack the facing benzene ring intramolecularly. The failure of the photocyclisation upon irradiation in aprotic solvents, such as acetone, acetonitrile, and benzene, supported the proposed reaction pathway *via* the protonated intermediate,[22] and the latter was evidenced by the experiment where the butenolide **5f** gave the tricycle **6f** efficiently upon irradiation in acetonitrile containing acetic acid.*

It is interesting to note that the efficiency of the intramolecular cycloaddition in substrates **5** is increased with increasing bulk of the substituents on the 'central carbon'. The Newman projection of compound **5f** shows that the phenyl and butenolide π planes on the 'central methane' are highly restricted in free rotation by the isopropyl methyls and are forced to cause easy linkage to afford the indenofuranone system.[2b] This speculation is supported by the fact that the butenolide olefinic protons in compounds **5e** and **5f** were deshielded, possibly by the anisotropy of the phenyl ring, and were shifted downfield in comparison with those of compounds **5a**–**5d** and **5g** (Table 2).

Table 2 Chemical shifts for olefinic protons in benzylic furan-2(5*H*)-ones **5a**–**g**

5a	6.93 (tt)	**5b**	7.02 (dt)	**5c**	7.08 (dt)
5d	7.08 (dt)	**5e**	7.21–7.23 (m)	**5f**	7.23–7.25 (m)
5g	6.96 (dt)				

A variety of aryl-vinyl-heterocycles based on the group VI elements or on nitrogen are known to photocyclise (hetero-atom-directed photoarylation) to give aryl-annelated heterocycles.[23] The present case is a rare example of cycloaddition in the homogeneous di-π-methane system, and provides us with a new route to the tetrahydroindenofuranone skeleton.

The di-π-methane rearrangement was effected only in the irradiation of compound **5g**. Even upon irradiation of substrates **5a**, **5b** and **5e** in acetone, no sign of the di-π-methane rearrangement was detected,† and acetone adducts **19a**, **19b** and **19e** and photoreduced products **7a**, **7b** and **7e** were formed as the main products. Presumably, one of the phenyl groups in compound **5g** only would satisfy the stereoelectronic requirements ‡ for the rearrangement, and readily caused di-π-methane rearrangement to give compound **18g**.

Further studies on migratory selectivity in compounds **1** from the viewpoint of stereoelectronic requirements are in progress.

Experimental

M.p.s. (Yanagimoto MP-S3 micro melting point apparatus) and b.p.s points are uncorrected. IR spectra were measured on

* Irradiation in acetone containing acetic acid also gave compound **6f** though in low yield (23%) due to the complexity of the reaction.

† The increased efficiency of the di-π-methane rearrangement of 4-benzylfuran-2(5*H*)-ones under aceton-photosensitised conditions has been described (ref.24).

‡ The stereoelectronic requirements for the di-π-methane rearrangement have been proposed by Zimmerman and co-workers: see ref. 3*a*.

a Shimadzu IR-435 grating infrared spectrophotometer. NMR spectra were recorded on either a JEOL JNM-GSX 270 (270 MHz ^{1}H, 67.5 MHz ^{13}C) or a JEOL JNM-GSX 500 (500 MHz ^{1}H, 125 MHz ^{13}C) spectrometer. Chemical shifts and coupling constants (J) are given in δ-values (ppm) and in hertz (Hz), respectively, and following abbreviations are used; sext = sextet, sept = septet. 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 were carried out 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. Petroleum spirit refers to the fraction boiling in the range 30–70 °C.

3-*Benzyltetrahydrofuran*-2-*one* **7a**.—A suspension of 5% palladium on carbon (300 mg) in acetic acid (20 cm^3) was pre-equilibrated with hydrogen. A solution of 3-benzylidenetetrahydrofuran-2-one[8] (**8a**; 2.0 g, 11.5 mmol) in acetic acid (10 cm^3) was added, and the mixture was hydrogenated at 50 °C and atmospheric pressure until the uptake of hydrogen ceased. The catalyst was filtered off, and the filtrate was evaporated to give an oil (2.08 g) which, on distillation at reduced pressure, gave compound **7a** (2.0 g, 99%) as an oil, b.p. 122–124 °C/2 mmHg (lit.,[8a] 123–129 °C/0.2–0.5 mmHg) (Found: C, 74.8; H, 6.8%; M$^+$, 176.0830. $C_{11}H_{12}O_2$ requires C, 74.98; H, 6.86%; M, 176.0837).

3-*Benzyl*-3-(*methylsulfanyl*)*tetrahydrofuran*-2-*one* **9a**.—Under argon, a 1.6 mol dm^{-3} solution of butyllithium in hexane (5.3 cm^3, 8.48 mmol) was added dropwise to a solution of *N*-isopropylcyclohexylamine (1.4 cm^3, 8.53 mmol) in THF (5 cm^3) at 0 °C, and the mixture was stirred at 0 °C for 10 min. A solution of compound **7a** (1.0 g, 5.68 mmol) in THF (10 cm^3) was added to the mixture, which was stirred for another 30 min. The lithium enolate thus prepared was added dropwise to a solution of dimethyl disulfide (1.5 cm^3, 17.0 mmol) in THF (5 cm^3) at 0 °C. After being stirred at 0 °C for 1 h, the reaction mixture was poured into brine (20 cm^3), and extracted with benzene. The extract was washed with brine, and evaporated to give an orange oil (1.1 g) which, on column chromatography (hexane–acetone, 20:1), gave the starting material **7a** (208 mg, 21% recovery) and *title sulfide* **9a** (726 mg, 58%) as prisms, m.p. 94–95 °C (from EtOH) (Found: C, 64.7; H, 6.35%; M$^+$, 222.0701. $C_{12}H_{14}O_2S$ requires C, 64.84; H, 6.35%; M, 222.0715); ν_{max}($CHCl_3$)/cm^{-1} 1758; δ_H 1.90 (1 H, ddd, J 13.5, 5.1 and 1.5), 2.26 (3 H, s), 2.44 (1 H, ddd, J 13.5, 10.7 and 9.0), 3.04 (1 H, d, J 14.0), 3.35 (1 H, d, J 14.0), 4.08 (1 H, ddd, J 9.0, 9.0 and 1.5), 4.34 (1 H, ddd, J 10.7, 9.0 and 5.1) and 7.20–7.33 (5 H, m); δ_C 11.9 (q), 33.3 (t), 39.6 (t), 49.5 (s), 65.0 (t), 127.1 (d), 128.4 (d), 130.2 (d), 135.6 (s) and 175.0 (s); m/z 222 (M$^+$, 15%), 176 (93), 131 (89) and 91 (100).

Sodium Metaperiodate Oxidation of Sulfide **9a**.—A mixture of sulfide **9a** (500 mg, 2.25 mmol), sodium metaperiodate (1.0 g, 4.67 mmol), THF (13 cm^3), and water (8 cm^3) was stirred at room temperature for 12 h. The resulting precipitates were filtered off, and the filtrate was poured into water (10 cm^3) and extracted with chloroform. The extract was washed with brine, and evaporated to give a pale yellow oil (485 mg), which was heated in toluene (10 cm^3) under reflux for 10 min. The mixture was washed with aq. sodium thiosulfate–sodium hydrogen carbonate, and evaporated to give a pale brown oil (447 mg) which, on column chromatography (hexane–acetone, 10:1), gave a 1:1 mixture‡ of 3-benzylfuran-2(5*H*)-one **5a** and its regioisomer **8a** as an oil (306 mg, 78%).

Methyl 3-*Benzyl*-4-(tert-*butyldimethylsiloxy*)-3-*hydroxybutanoate* **11**.—Under argon, a 1.6 mol dm^{-3} solution of butyllithium in hexane (11.2 cm^3, 17.9 mmol) was added dropwise to a solution of diisopropylamine (2.5 cm^3, 17.9 mmol) in THF (20 cm^3) at 0 °C, and the mixture was stirred at 0 °C for 10 min. The mixture was cooled to −50 °C, and hexamethylphosphoric triamide (HMPA) (4.2 cm^3, 24.2 mmol) was added. To the mixture was added a solution of methyl 4-(*tert*-butyldimethylsiloxy)-3-hydroxybutanoate[10] **10** (2.0 g, 8.1 mmol) in THF (10 cm^3) at −60 to −50 °C, and the resulting mixture was stirred at that temperature for 30 min. After addition of a solution of benzyl bromide (1.2 cm^3, 10 mmol) in THF (5 cm^3) followed by stirring of the mixture at −20 °C for 1 h, the mixture was poured into ice–water (100 cm^3) and extracted with dichloromethane. The extract was washed with brine and evaporated to give an orange oil (6.8 g), which, on column chromatography ($CHCl_3$), gave *compound* **11** (1.16 g, 43%) as an oil, b.p. 128–130 °C/0.008 mmHg (Found: M$^+$, 338.1896. $C_{18}H_{30}O_4Si$ requires M, 338.1913); ν_{max}($CHCl_3$)/cm^{-1} 3541 and 1729; δ_H 0.04 (3 H, s), 0.05 (3 H, s), 0.89 (9 H, s), 2.85–3.02 (3 H, m), 3.04 (1 H, d, J 8.0, exchangeable with D_2O), 3.59 (3 H, s), 3.64 (1 H, dd, J 11.0 and 5.0), 3.66 (1 H, dd, J 11.0 and 5.0), 3.75 (1 H, m) and 7.16–7.31 (5 H, m); δ_C −5.6 (q), 18.2 (s), 25.7 (q), 35.2 (t), 49.5 (d), 51.4 (q), 65.2 (t), 71.8 (d), 126.4 (d), 128.2 (d), 128.8 (d), 138.5 (s) and 174.7 (s); m/z 338 (M$^+$, 0.3%), 281 (67), 249 (57), 117 (100) and 91 (41).

cis-3-*Benzyl*-4-*hydroxytetrahydrofuran*-2-*one* **12**.—A mixture of siloxy ester **11** (850 mg, 2.5 mmol), 10% hydrochloric acid (5 cm^3), and DME (8 cm^3) was heated at 80 °C for 30 min. After removal of the solvent, the residue was extracted with CH_2Cl_2. The extract was washed with brine, and evaporated to give a solid (490 mg) which, on column chromatography ($CHCl_3$), gave *lactone* **12** (411 mg, 85%) as prisms, m.p. 63–65 °C (from cyclohexane) (Found: C, 68.7; H, 6.3%; M$^+$, 192.0762. $C_{11}H_{12}O_3$ requires C, 68.73; H, 6.29%; M, 192.0786); ν_{max}($CHCl_3$)/cm^{-1} 3420 and 1776; δ_H 2.30 (1 H, br s, exchangeable with D_2O), 2.83 (1 H, ddd, J 11.5, 4.0 and 4.0), 2.98 (1 H, dd, J 14.5 and 11.5), 3.21 (1 H, dd, J 14.5 and 4.0) 4.27 (1 H, dd, J 10.0 and 3.0), 4.29 (1 H, d, J 10.0), 4.41 (1 H, dd, J 4.0 and 3.0) and 7.22–7.35 (5 H, m); δ_C 29.3 (t), 47.3 (d), 68.7 (t), 74.4 (d), 126.7 (d), 128.6 (d), 128.8 (d), 138.8 (s) and 177.1 (s); m/z 192 (M$^+$, 72%), 148 (96), 131 (69) and 91 (100).

3-*Benzylfuran*-2(5H)-*one* **5a**.—Phosphorus trichloride oxide (0.7 cm^3, 7.5 mmol) was added to a stirred solution of the alcohol **12** (300 mg, 1.56 mmol) in pyridine (5 cm^3) at 0 °C. After being stirred at 0 °C for 1 h, the reaction mixture was poured into ice–water (30 cm^3), acidified with 10% sulfuric acid, and extracted with diethyl ether. The extract was washed with brine and evaporated to give an oil (278 mg) which, on column chromatography (hexane–acetone, 1:1), gave compound **5a** (257 mg, 95%) as an oil, b.p. 141–143 °C/0.01 mmHg (lit.,[7c] 114 °C/0.2 mmHg) (Found: C, 75.6; H, 5.8%; M$^+$, 174.0682. $C_{11}H_{10}O_2$ requires C, 75.84; H, 5.79%; M, 174.0681).

Stobbe Condensation of Diethyl Succinate with Ketones.—1-*Ethyl* 4-*hydrogen* 2-(1-*phenylethylidene*)*succinate* **13b**. A mixture of acetophenone (18.0 g, 150 mmol), diethyl succinate (40.0 g, 230 mmol), and benzene (50 cm^3) was added dropwise to a

‡ The ratio of the products was determined on the basis of the ^{1}H NMR spectrum.

suspension of sodium hydride (6.0 g, 150 mmol; 60% in liquid paraffin; washed twice with benzene) in benzene (100 cm^3) at 0 °C, and to the resulting mixture was added dropwise absolute ethanol (2 cm^3) at that temperature. After being stirred at room temperature for 1 h, the reaction mixture was poured into ice-cooled water (300 cm^3), and washed with diethyl ether. The aqueous layer was acidified with 10% sulfuric acid, and extracted with diethyl ether, and the extract was re-extracted with aq. sodium hydrogen carbonate. The aqueous extract was acidified with 10% sulfuric acid, and extracted with diethyl ether. This extract was washed with brine and evaporated to give a 1:1 isomeric mixture‡ of (*E*)- and (*Z*)-**13b** (34.5 g) as a pale yellow semi-solid, which was used in the next step without purification. An analytical sample of compound (*Z*)-**13b** was obtained as prisms by trituration of the semi-solid with a mixture of diethyl ether and petroleum spirit followed by recrystallisation from benzene–petroleum spirit.

(*Z*)-**13b**: m.p. 108–109 °C (lit.,[13a] 111–112 °C) (Found: C, 67.6; H, 6.5. $C_{14}H_{16}O_4$ requires C, 67.73; H, 6.50%); ν_{max}($CHCl_3$)/cm^{-1} 2620 and 1710; δ_H 0.79 (3 H, t, *J* 7.0), 2.16 (3 H, s), 3.57 (2 H, s), 3.86 (2 H, q, *J* 7.0), 7.12–7.16 (2 H, m), 7.26–7.43 (3 H, m) and 9.0–10.5 (1 H, br); δ_C 13.3 (q), 22.9 (q), 35.9 (t), 60.6 (t), 122.6 (s), 126.6 (d), 127.3 (d), 127.9 (d), 143.5 (s), 149.6 (s), 169.6 (s) and 176.1 (s). The *Z* configuration was assigned on the basis of difference NOE experiments in the present study.*

The other half-ester [(*E*)-**13b**] proved to be difficultly separable, so small amount of the crude mixture was treated with an ethereal solution of diazomethane to give a 1:1 mixture‡ of (*E*)- and (*Z*)-1-*ethyl* 4-*methyl* 2-(1-*phenylethylidene*)*succinate* (**13b** *Methyl ester*), which was separated on column chromatography (hexane–ethyl acetate, 30:1).

(E)-**13b** *Methyl ester*: *oil*, b.p. 86–88 °C/0.06 mmHg (Found: M^+, 262.1216. $C_{15}H_{18}O_4$ requires M, 262.1205); ν_{max}($CHCl_3$)/cm^{-1} 1731 and 1629; δ_H 1.31 (3 H, t, *J* 7.0), 2.42 (3 H, s), 3.19 (2 H, s), 3.65 (3 H, s), 4.25 (2 H, q, *J* 7.0), 7.12–7.17 (2 H, m) and 7.26–7.43 (3 H, m); δ_C 14.0 (q), 23.5 (q), 36.7 (t), 51.6 (q), 60.3 (t), 122.3 (s), 126.6 (d), 127.4 (d), 128.4 (d), 145.8 (s), 151.9 (s), 167.5 (s) and 171.9 (s); *m*/*z* 262 (M^+, 2%), 216 (76), 188 (25) and 129 (100).

(Z)-**13b** *Methyl ester*: *oil*, b.p. 83–85 °C/0.06 mmHg (Found: M^+, 262.1204. $C_{15}H_{18}O_4$ requires M, 262.1205); ν_{max}($CHCl_3$)/cm^{-1} 1735 and 1698; δ_H 0.80 (3 H, t, *J* 7.0), 2.14 (3 H, s), 3.54 (2 H, s), 3.72 (3 H, s), 3.85 (2 H, q, *J* 7.0), 7.12–7.17 (2 H, m) and 7.26–7.34 (3 H, m); δ_C 13.3 (q), 22.7 (q), 35.7 (t), 52.0 (q), 60.3 (t), 123.5 (s), 126.7 (d), 127.2 (d), 127.9 (d), 143.7 (s), 148.5 (s), 168.7 (s) and 171.2 (s); *m*/*z* 262 (M^+, 2%), 216 (68), 188 (26) and 129 (100).

(E)-1-*Ethyl* 4-*hydrogen* 2-(*cyclohexylphenylmethylene*)*succinate* (E)-**13e** [15.2 g, 90% yield from cyclohexyl phenyl ketone (10.0 g, 53 mmol)]: *needles* m.p. 138–139 °C (from benzene–petroleum spirit) (lit.,[13b] 120–121 °C) (Found: C, 72.1; H, 7.6. $C_{19}H_{24}O_4$ requires C, 72.12; H, 7.65%); δ_H 0.90–1.04 (3 H, m), 1.32 (3 H, t, *J* 7.0), 1.27–1.37 (2 H, m), 1.58 (1 H, br d, *J* 13.0), 1.65–1.77 (4 H, m), 3.01 (2 H, s), 3.42 (1 H, tt, *J* 12.5 and 3.0), 4.27 (2 H, q, *J* 7.0), 6.97–7.00 (2 H, m) and 7.28–7.36 (3 H, m); δ_C 14.1 (q), 25.8 (t), 26.2 (t), 31.5 (t), 37.1 (t), 42.0 (d), 60.7 (t), 121.7 (s), 127.2 (d), 127.6 (d), 128.0 (d), 138.7 (s), 160.5 (s), 167.8 (s) and 177.3 (s). The *E* configuration was assigned on the basis of difference NOE experiments in the present study.

(E)-1-*Ethyl* 4-*hydrogen* 2-(2-*methyl*-1-*phenylpropylidene*)-*succinate* (E)-**13f** [21.2 g, 90% yield from isopropyl phenyl ketone (12.6 g, 85 mmol)]: *prisms*, m.p. 125.5–126 °C (from benzene–petroleum spirit) (lit.,[13c] 121–122 °C) (Found: C, 69.5; H, 7.3. $C_{16}H_{20}O_4$ requires C, 69.54; H, 7.30%); δ_H 0.96 (6 H, d, *J* 7.0), 1.30 (3 H, t, *J* 7.0), 3.02 (2 H, s), 3.78 (1 H, sept, *J* 7.0), 4.26 (2 H, q, *J* 7.0), 6.99–7.02 (2 H, m) and 7.28–7.37 (3 H, m); δ_C 14.0 (q), 21.2 (q), 31.1 (d), 37.1 (t), 60.7 (t), 121.7 (s), 127.2 (d), 127.9 (d), 128.0 (d), 137.8 (s), 160.8 (s), 167.8 (s) and 177.1 (s).

1-*Ethyl* 4-*hydrogen* 2-(*diphenylmethylene*)*succinate* **13g** [29.1 g, 95% yield from benzophenone (18.0 g, 99 mmol)]: *needles*, m.p. 126–127 °C (from benzene–light petroleum) (lit.,[13a] 124.5–125.5 °C (Found: C, 73.3; H, 5.9. $C_{19}H_{18}O_4$ requires C, 73.53; H, 5.85%); ν_{max}($CHCl_3$)/cm^{-1} 2640 and 1709; δ_H 0.87 (3 H, t, *J* 7.0), 3.53 (2 H, s), 3.97 (2 H, q, *J* 7.0) and 7.10–7.39 (10 H, m); δ_C 13.3 (q), 37.9 (t), 60.8 (t), 124.3 (s), 127.8 (d), 127.9 (d), 128.3 (d), 128.4 (d), 128.6 (d), 129.0 (d), 140.4 (s), 142.0 (s), 152.5 (s), 169.3 (s) and 177.7 (s).

1-*Ethyl* 4-*hydrogen* 2-(1-*phenylpropylidene*)*succinate* **13c** *and* 1-*Ethyl* 4-*hydrogen* 2-(1-*phenylprop*-1-*enyl*)*succinate* **14a**. A 1:1:2.8:7 mixture‡ of compounds (E)-**13c**, (*Z*)-**13c**, (*E*)-**14a** and (*Z*)-**14a** (9.8 g) was obtained from propiophenone (5.0 g, 37 mmol) as a pale yellow oil, which was used in the next step without purification.

For the structural identification, a small amount of the oil was treated with an ethereal solution of diazomethane to give the corresponding ethyl methyl succinates which, on column chromatography (hexane–ethyl acetate, 40:1), gave (Z)-1-*ethyl* 4-*methyl* 2-(1-*phenylpropylidene*)*succinate* (Z)-**13c** *methyl ester*,§ (Z)-1-*ethyl* 4-*methyl* 2-(1-*phenylprop*-1-*enyl*)*succinate* (Z)-**14a** *methyl ester*,† and a 1:3 mixture‡ of (*E*)-**13c** methyl ester§ and (*E*)-**14a** methyl ester.

(Z)-**13c** *Methyl ester*: *oil*, b.p. 89–91 °C/0.06 mmHg (Found: M^+, 276.1360. $C_{16}H_{20}O_4$ requires M, 276.1361); ν_{max}($CHCl_3$)/cm^{-1} 1736 and 1697; δ_H 0.78 (3 H, t, *J* 7.0), 0.94 (3 H, t, *J* 7.0), 2.48 (2 H, q, *J* 7.0), 3.54 (2 H, s), 3.72 (3 H, s), 3.83 (2 H, q, *J* 7.0), 7.09–7.15 (2 H, m) and 7.25–7.35 (3 H, m); δ_C 11.9 (q), 13.4 (q), 29.1 (t), 35.1 (t), 52.0 (q), 60.3 (t), 123.0 (s), 127.1 (d), 127.3 (d), 127.8 (d), 142.1 (s), 153.8 (s), 168.9 (s) and 171.4 (s); *m*/*z* 276 (M^+, 0.3%), 230 (83), 202 (40), 143 (100) and 128 (43).

(Z)-**14a** *Methyl ester*: *oil*, b.p. 92–94 °C/0.06 mmHg (Found: M^+, 276.1360); ν_{max}($CHCl_3$)/cm^{-1} 1726; δ_H 1.22 (3 H, t, *J* 7.0), 1.53 (3 H, d, *J* 7.0), 2.50 (1 H, dd, *J* 17.0 and 5.1), 2.85 (1 H, dd, *J* 17.0 and 10.0), 3.64 (3 H, s), 3.79 (1 H, dd, *J* 10.0 and 5.1), 4.15 (2 H, q, *J* 7.0), 5.74 (1 H, q, *J* 7.0), 7.08–7.14 (2 H, m) and 7.22–7.37 (3 H, m); δ_C 14.1 (q), 14.8 (q), 35.8 (t), 49.4 (d), 51.7 (q), 60.8 (t), 125.3 (d), 127.1 (d), 128.2 (d), 128.9 (d), 138.1 (s), 138.8 (s), 172.3 (s) and 172.8 (s); *m*/*z* 276 (M^+, 12%), 230 (62), 203 (95), 143 (88) and 128 (100).

A mixture of (*E*)-**13c** methyl ester and (*E*)-**14a** methyl ester had δ_H 1.00 (0.75 H, t, *J* 7.0), 1.19 (2.25 H, t, *J* 7.0), 1.32 (0.75 H, t, *J* 7.0), 1.88 (2.25 H, d, *J* 7.0), 2.38 (0.75 H, dd, *J* 17.0 and 5.0), 2.79 (0.5 H, q, *J* 7.0), 3.04 (0.75 H, dd, *J* 17.0 and 10.0), 3.14 (0.5 H, s), 3.62 (0.75 H, s), 3.66 (2.25 H, s), 4.14 (0.75 H, dq, *J* 11.0 and 7.0), 4.18 (0.75 H, dq, *J* 11.0 and 7.0), 4.26 (0.5 H, q, *J* 7.0), 4.30 (0.75 H, dd, *J* 10.0 and 5.0), 5.70 (0.75 H, t, *J* 7.0) and 7.08–7.38 (5 H, m); δ_C 12.5 (q), 14.0 (q), 14.1 (q), 14.2 (q), 29.6 (t), 34.7 (t), 37.0 (t), 42.3 (d), 51.7 (q), 51.8 (q), 60.5 (t), 61.1 (t), 122.1 (s), 126.9 (d), 127.2 (d), 127.3 (d), 127.5 (d), 128.1 (d), 128.2 (d), 128.4 (d), 137.7 (s), 141.4 (s), 141.7 (s), 157.4 (s), 167.7 (s), 172.0 (s), 172.4 (s) and 173.0 (s). The two regioisomers (*E*)-**13c** *methyl*

‡ See footnote on p. 1837.

* The configuration of compound (*Z*)-**13b** was determined on the basis of the ^1H NMR spectrum of the corresponding methyl ester which was obtained by treatment with an ethereal solution of diazomethane.

† The *Z*-configuration was determined on the basis of the significant upfield shift of the signal due to the methyl of the ethylidene moiety, resulting from the anisotropy of the phenyl group.

§ The configurations of the phenyl ring in **13c**-esters and **13d**-esters were determined to be the same as those in **13b**-esters on the basis of the similar features for the α-methylene protons in their ^1H NMR spectra.

ester and (*E*)-**14a** *methyl ester* were separated by GC-MS; for the major isomer (E)-**14a** *methyl ester* (Found: M^+, 276.1357); *m/z* 276 (M^+, 17%), 230 (55), 203 (85), 143 (79) and 128 (100). For the minor isomer (E)-**13c** *methyl ester* (Found: M^+, 276.1366); *m/z* 276 (M^+, 0.3%), 230 (87), 202 (36), 143 (100) and 128 (44).

1-*Ethyl* 4-*hydrogen* 2-(1-*phenylbutylidene*)*succinate* **13d** *and* 1-*ethyl* 4-*hydrogen* 2-(1-*phenylbut*-1-*enyl*)*succinate* **14b**. A 1:1:1.8:3.5 mixture‡ of compounds (*E*)-**13d**, (*Z*)-**13d**, (*E*)-**14b** and (*Z*)-**14b** (13.8 g) was obtained from butyrophenone (7.0 g, 47 mmol) as a pale yellow oil, which was used in the next step without purification.

For the structural identification, (Z)-1-*ethyl* 4-*methyl* 2-(1-*phenylbutylidene*)*succinate* (*Z*)-**13d** *methyl ester*,§ (Z)-1-*ethyl* 4-*methyl* 2-(1-*phenylbut*-1-*enyl*)*succinate* (Z)-**14b** *methyl ester*, and a 1:2 mixture‡ of (*E*)-**13d** methyl ester§ and (*E*)-**14b** methyl ester were obtained following a method similar to that described above.

(Z)-**13d** *Methyl ester*: *oil*, b.p. 112–114 °C/0.06 mmHg (Found: M^+, 290.1535. $C_{17}H_{22}O_4$ requires M, 290.1518); $\nu_{max}(CHCl_3)/cm^{-1}$ 1736 and 1698; δ_H 0.77 (3 H, t, *J* 7.0), 0.87 (3 H, t, *J* 7.0), 1.32 (2 H, sext-like, *J* 7.0), 2.44 (2 H, m), 3.55 (2 H, s), 3.71 (3 H, s), 3.82 (2 H, q, *J* 7.0), 7.09–7.15 (2 H, m) and 7.23–7.34 (3 H, m); δ_C 13.3 (q), 13.9 (q), 20.6 (t), 35.3 (t), 37.7 (t), 52.0 (q), 60.2 (t), 123.7 (s), 127.1 (d), 127.3 (d), 127.8 (d), 142.3 (s), 152.2 (s), 168.9 (s) and 171.4 (s); *m/z* 290 (M^+, 0.5%), 244 (100), 216 (38) and 157 (38).

(Z)-**14b** *Methyl ester*: *oil*, b.p. 114–116 °C/0.06 mmHg (Found: M^+, 290.1521); $\nu_{max}(CHCl_3)/cm^{-1}$ 1727; δ_H 0.89 (3 H, t, *J* 7.0), 1.22 (3 H, t, *J* 7.0), 1.89 (2 H, dq, *J* 7.0 and 7.0), 2.52 (1 H, dd, *J* 17.0 and 5.5), 2.85 (1 H, dd, *J* 17.0 and 10.0), 3.64 (3 H, s), 3.77 (1 H, dd, *J* 10.0 and 5.5), 4.13 (1 H, dq, *J* 11.0 and 7.0), 4.17 (1 H, dq, *J* 11.0 and 7.0), 5.62 (1 H, t, *J* 7.0), 7.08–7.14 (2 H, m) and 7.22–7.36 (3 H, m); δ_C 14.07 (q), 14.13 (q), 22.4 (t), 35.8 (t), 49.3 (d), 51.7 (q), 60.8 (t), 127.1 (d), 128.1 (d), 128.8 (d), 132.8 (d), 136.8 (s), 139.1 (s), 172.3 (s) and 172.8 (s); *m/z* 290 (M^+, 9%), 185 (56), 157 (44), 142 (100) and 131 (59). The *Z* configuration was assigned on the basis of difference NOE experiments in the present study.

A mixture of (*E*)-**13d** methyl ester and (*E*)-**14b** methyl ester had δ_H 0.89 (1 H, t, *J* 7.0), 1.08 (2 H, t, *J* 7.0), 1.19 (2 H, t, *J* 7.0), 1.31 (1 H, t, *J* 7.0), 1.40 (0.66 H, sext-like, *J* 7.0), 2.18–2.44 (1.33 H, m), 2.37 (1.33 H, dd, *J* 17.0 and 5.0), 2.76 (0.66 H, m), 3.02 (0.66 H, dd, *J* 17.0 and 9.5), 3.15 (0.66 H, s), 3.63 (1 H, s), 3.65 (2 H, s), 4.15 (0.66 H, q, *J* 7.0), 4.25 (0.66 H, q, *J* 7.0), 4.28 (0.66 H, dd, *J* 9.5 and 5.0), 5.70 (0.66 H, t, *J* 7.0) and 7.08–7.38 (5 H, m); δ_C 13.87 (q), 13.94 (q), 14.0 (q), 14.1 (q), 21.2 (t), 21.9 (t), 35.0 (t), 37.0 (t), 38.1 (t), 42.5 (d), 51.69 (q), 51.73 (q), 60.5 (t), 61.1 (t), 122.6 (s), 126.9 (d), 127.2 (d), 127.3 (d), 127.4 (d), 128.1 (d), 128.4 (d), 135.9 (d), 136.1 (s), 141.65 (s), 141.71 (s), 155.9 (s), 167.8 (s), 172.0 (s), 172.4 (s) and 173.0 (s). The two regioisomers (*E*)-**13d** methyl ester and (*E*)-**14b** methyl ester were separated by GC-MS; for the major isomer (E)-**14b** *methyl ester* (Found: M^+, 290.1537); *m/z* 290 (M^+, 12%), 185 (52), 157 (41), 142 (100) and 131 (58). For the minor isomer (E)-**13d** *methyl ester* (Found: M^+, 290.1535); *m/z* 290 (M^+, 0.1%), 244 (100), 216 (35) and 157 (38).

Preparation of 3-(α-*Substituted Benzylidene*)*tetrahydrofuran*-2-*ones* **8**.—3-(1-*Phenylethylidene*)*tetrahydrofuran*-2-*one* **8b**. A 10 mol dm^{-3} solution of BMS (7.0 cm^3, 70 mmol) in THF was injected slowly into a stirred solution of half-ester **13b** (8.7 g, 35.1 mmol) in THF (40 cm^3) at 0 °C, and the resulting mixture was stirred at 0 °C for 3 h. To the mixture were added successively dropwise water (25 cm^3) and saturated aq. sodium hydrogen carbonate (25 cm^3), and the mixture was extracted with chloroform. The extract was washed with brine and evaporated to give an orange oil (8.25 g), which was used in the next step without purification.

The oil (8.25 g) was dissolved in a mixture of 10% hydrochloric acid–DME (60 cm^3; 1:5), and the resulting mixture was heated under reflux for 1 h, and concentrated under reduced pressure. The residue was extracted with diethyl ether, and the extract was washed with brine, and evaporated to give an orange oil (6.45 g) which, on column chromatography ($CHCl_3$), gave a 1:1 mixture‡ of compounds (*E*)-**8b** and (*Z*)-**8b** (4.35 g, 66%) as a pale yellow oil, b.p. 145–148 °C/2 mmHg (lit.,[8b] 120 °C/0.2 mmHg; lit.,[8c] 130–135 °C/0.1 mmHg) (Found: M^+, 188.0830. $C_{12}H_{12}O_2$ requires M, 188.0837).

(E)-3-(α-*Cyclohexylphenylmethylene*)*tetrahydrofuran*-2-*one* (E)-**8e** [2.8 g, 69% yield from (*E*)-**13e** (5.0 g, 15.8 mmol)]: *needles*, m.p. 105–106 °C (from hexane) (Found: C, 79.45; H, 7.9%; M^+, 256.1441. $C_{17}H_{20}O_2$ requires C, 79.65; H, 7.86%; M, 256.1463); $\nu_{max}(CHCl_3)/cm^{-1}$ 1743 and 1640; δ_H 0.98 (1 H, ddddd, *J* 13.0, 13.0, 13.0, 3.5 and 3.5), 1.07 (2 H, dddd, *J* 13.0, 13.0, 13.0 and 3.0), 1.41 (2 H, ddddd, *J* 13.0, 13.0, 13.0, 3.0 and 3.0), 1.57–1.72 (5 H, m), 2.50 (2 H, t, *J* 7.5), 4.10 (1 H, dddd, *J* 13.0, 13.0, 3.0 and 3.0), 4.20 (2 H, t, *J* 7.5), 6.99–7.03 (2 H, m), 7.29–7.34 (1 H, m) and 7.36–7.40 (2 H, m); δ_C 25.8 (t), 26.1 (t), 29.0 (t), 31.1 (t), 38.5 (d), 64.7 (t), 120.1 (s), 126.7 (d), 127.8 (d), 128.4 (d), 139.7 (s), 162.0 (s) and 170.0 (s); *m/z* 256 (M^+, 57%), 174 (43), 129 (100), 115 (16) and 91 (15).

(E)-3-(2-*Methyl*-1-*phenylpropylidene*)*tetrahydrofuran*-2-*one* (E)-**8f** [3.1 g, 66% yield from (*E*)-**13f** (6.0 g, 21.7 mmol)]: *oil*, b.p. 110–112 °C/0.01 mmHg (Found: C, 77.6; H, 7.4%; M^+, 216.1158. $C_{14}H_{16}O_2$ requires C, 77.75; H, 7.46%; M, 216.1150); $\nu_{max}(CHCl_3)/cm^{-1}$ 1740 and 1642; δ_H 0.99 (6 H, d, *J* 7.0), 2.51 (2 H, t, *J* 7.5), 4.21 (2 H, t, *J* 7.5), 4.47 (1 H, sept, *J* 7.0) and 7.29–7.44 (5 H, m); δ_C 20.9 (q), 27.8 (d), 28.9 (t), 64.6 (t), 120.0 (s), 126.9 (d), 127.3 (d), 128.3 (d), 138.8 (s), 162.2 (s) and 169.9 (s); *m/z* 216 (M^+, 100%), 129 (39), 115 (26) and 91 (26).

3-(*Diphenylmethylene*)*tetrahydrofuran*-2-*one* **8g** [20.3 g, 87% yield from **13g** (29.0 g, 93.5 mmol)]: *needles*, m.p. 171–172 °C (from EtOH) (lit.,[8c] 175–176 °C; lit.[14a] 169–170 °C; lit.,[14b] 178–179 °C; lit.,[14c] 167.5–169.5 °C) (Found: C, 81.4; H, 5.7%; M^+, 250.1006. $C_{17}H_{14}O_2$ requires C, 81.58; H, 5.64%; M, 250.0993).

Preparation of 3-(α-*Substituted Benzyl*)*tetrahydrofuran*-2-*ones* **7b**, **7e**, **7f** and **7g**.—Following a method similar to that used for the preparation of compound **7a**, catalytic hydrogenation of the corresponding tetrahydrofuranone **8** was carried out.

3-(1-*Phenylethyl*)*tetrahydrofuran*-2-*one* **7b** [2.6 g, 86% yield as a 1:1 diastereoisomeric mixture‡ from **8b** (3.0 g, 16.0 mmol)]: *oil*, b.p. 145–147 °C/0.01 mmHg (Found: M^+, 190.0983. $C_{12}H_{14}O_2$ requires M, 190.0994); $\nu_{max}(CHCl_3)/cm^{-1}$ 1763; δ_H 1.35 (1.5 H, d, *J* 7.0), 1.50 (1.5 H, d, *J* 7.0), 1.87 (0.5 H, dddd, *J* 13.0, 9.0, 9.0 and 9.0), 2.12 (0.5 H, dddd, *J* 13.0, 9.0, 7.0 and 4.5), 2.13 (0.5 H, dddd, *J* 13.0, 9.5, 7.5 and 4.0), 2.22 (0.5 H, dddd, *J* 13.0, 9.5, 9.0 and 9.0), 2.75 (0.5 H, ddd, *J* 9.0, 9.0 and 7.0), 2.87 (0.5 H, ddd, *J* 9.5, 9.5 and 4.5), 3.26 (0.5 H, dq, *J* 7.0 and 7.0), 3.44 (0.5 H, qd, *J* 7.0 and 4.5), 3.93 (0.5 H, ddd, *J* 9.0, 9.0 and 4.5), 4.07 (0.5 H, ddd, *J* 9.0, 9.0 and 7.5), 4.10 (0.5 H, ddd, *J* 9.0, 9.0 and 7.0), 4.15 (0.5 H, ddd, *J* 9.0, 9.0 and 4.0), 7.21–7.27 (3 H, m) and 7.28–7.35 (2 H, m); δ_C 15.5/19.8 (q), 24.2/26.0 (t), 38.6/39.6 (d), 45.8/45.9 (d), 66.3/66.4 (t), 126.8 (d), 126.9 (d), 127.2 (d), 127.7 (d), 128.5 (d), 128.6 (d), 142.8/143.6 (s) and 178.0/178.3 (s); *m/z* 190 (M^+, 19%), 105 (100), 91 (8) and 86 (22).

3-(α-*Cyclohexylphenylmethyl*)*tetrahydrofuran*-2-*one* **7e** [955 mg, 95% yield as a 7:1 diastereoisomeric mixture‡ from **8e** (1.0

‡ See footnote on p. 1837.
§ See footnote on p. 1838.

g, 3.91 mmol)]: *oil*, b.p. 165–167 °C/0.05 mmHg (Found: M^+, 258.1627. $C_{17}H_{22}O_2$ requires M, 258.1620); $\nu_{max}(CHCl_3)/cm^{-1}$ 1759; δ_H 0.68–0.84 (1 H, m), 0.97–1.20 (3 H, m), 1.29–1.41 (2 H, m), 1.54–1.68 (3 H, m), 1.74–1.82 (1 H, m), 2.00–2.17 (2 H, m), 2.20 (0.13 H, dddd, *J* 12.5, 9.0, 8.0 and 4.8), 2.30 (0.87 H, dddd, *J* 12.5, 9.0, 8.0 and 4.8), 2.65 (0.87 H, dd, *J* 10.5 and 4.0), 2.98 (0.13 H, dd, *J* 9.0 and 5.5), 3.03 (0.87 H, ddd, *J* 9.0, 9.0 and 4.0), 3.10 (0.13 H, ddd, *J* 9.0, 9.0 and 5.5), 3.66 (0.87 H, ddd, *J* 9.0, 9.0 and 4.8), 3.81 (0.13 H, ddd, *J* 8.6, 8.6 and 4.8), 4.01 (0.87 H, ddd, *J* 9.0, 8.0 and 8.0), 4.06 (0.13 H, ddd, *J* 8.6, 8.0 and 8.0) and 7.16–7.32 (5 H, m); δ_C (minor isomer/major isomer) 24.5 (t), 26.1 (t), 26.17 (t), 26.22 (t), 26.3 (t), 26.4 (t), 30.8/31.6 (t), 31.5/32.0 (t), 38.2/38.4 (d), 41.1/41.0 (d), 50.9/53.0 (d), 66.5/66.3 (t), 126.8 (d), 128.2 (d), 128.6 (d), 129.6 (d), 139.2/141.9 (s) and 179.0/178.2 (s); *m/z* 258 (M^+, 17%), 172 (86), 148 (100), 91 (72) and 86 (49).

3-(2-*Methyl*-1-*phenylpropyl*)*tetrahydrofuran*-2-*one* **7f** [2.45 g, 90% yield as a 4:1 diastereoisomeric mixture‡ from **8f** (2.7 g, 12.5 mmol)]: *oil*, b.p. 142–143 °C/0.005 mmHg (Found: M^+, 218.1279. $C_{14}H_{18}O_2$ requires M, 218.1307); $\nu_{max}(CHCl_3)/cm^{-1}$ 1763; δ_H 0.70 (2.4 H, d, *J* 6.2), 0.82 (0.6 H, d, *J* 6.2), 1.03 (0.6 H, *J* 6.2), 1.12 (2.4 H, d, *J* 6.2), 1.99–2.07 (0.8 H, m), 2.16–2.26 (0.2 H, m), 2.27–2.35 (1.2 H, m), 2.47–2.56 (1.6 H, m), 2.92 (0.2 H, dd, *J* 9.0 and 6.5), 3.05 (0.8 H, ddd, *J* 9.5, 8.0 and 4.0), 3.08 (0.2 H, m), 3.61 (0.8 H, ddd, *J* 9.0, 9.0 and 5.0), 3.82 (0.2 H, ddd, *J* 8.5 and 4.8), 4.01 (0.8 H, ddd, *J* 9.0, 8.0 and 8.0), 4.06 (0.2 H, ddd, *J* 9.0 and 7.5) and 7.17–7.32 (5 H, m); δ_C (minor isomer/major isomer) 20.4/21.4 (q), 21.3/21.8 (q), 24.6/26.4 (t), 28.7/29.3 (d), 41.9/41.5 (d), 52.0/54.5 (d), 66.4/66.3 (t), 126.8 (d), 126.9 (d), 128.1 (d), 128.6 (d), 129.5 (d), 139.1/141.8 (s) and 178.8/178.2 (s); *m/z* 218 (M^+, 19%), 148 (70), 131 (92), 91 (100) and 86 (92).

3-*Benzhydryltetrahydrofuran*-2-*one* **7g** [1.93 g, 96% yield from **8g** (2.0 g, 8.0 mmol)]: *prisms*, m.p. 78–79 °C (from EtOH) (Found: C, 80.8; H, 6.6%; M^+, 252.1138. $C_{17}H_{16}O_2$ requires C, 80.93; H, 6.39%; M, 252.1151); $\nu_{max}(CHCl_3)/cm^{-1}$ 1765; δ_H 2.15 (1 H, dddd, *J* 13.0, 9.0, 8.0 and 8.0), 2.46 (1 H, dddd, *J* 13.0, 9.0, 8.0 and 4.5), 3.44 (1 H, ddd, *J* 9.0, 9.0 and 5.0), 3.90 (1 H, ddd, *J* 9.0, 9.0 and 4.5), 4.17 (1 H, ddd, *J* 9.0, 8.0 and 8.0), 4.70 (1 H, d, *J* 5.0) and 7.16–7.38 (10 H, m); δ_C 26.2 (t), 43.5 (d), 50.5 (d), 66.3 (t), 126.7 (d), 126.9 (d), 128.2 (d), 128.5 (d), 129.0 (d), 141.2 (s), 142.1 (s) and 178.1 (s); *m/z* 252 (M^+, 22%), 167 (100) and 152 (17).

Preparation of 3-(α-*Substituted Benzyl*)*tetrahydrofuran*-2-*ones* **7c** *and* **7d**.—3-(1-*Phenylpropyl*)*tetrahydrofuran*-2-*one* **7c**. Following a method similar to that used for the preparation of compound **7a**, a mixture of compounds **13c** and **14a** (3.0 g, 11.5 mmol) was hydrogenated to give a pale yellow oil (3.1 g). To a mixture of the oil (3.1 g), triethylamine (1.7 cm^3, 12.2 mmol), and THF (50 cm^3) was added a solution of ethyl chloroformate (1.63 cm^3, 17.1 mmol) in THF (5 cm^3) at 0 °C, and the mixture was stirred at 0 °C for 30 min. The resulting precipitates were filtered off, and washed with THF (10 cm^3). The combined filtrate and washings were added to a solution of sodium borohydride (1.3 g, 34.4 mmol) in water (20 cm^3) at 0 °C, and the mixture was stirred for 2 h. The reaction mixture was acidified with 10% sulfuric acid, heated under reflux for 3 h, and concentrated under reduced pressure. The residue was extracted with diethyl ether, and the extract was washed with brine. The combined extract was evaporated to give a pale yellow oil (2.4 g), which, on distillation at reduced pressure, gave a 2:1 diastereoisomeric mixture‡ of compound **7c** (2.0 g, 86%) as an oil, b.p. 141–143 °C/0.006 mmHg (Found: M^+, 204.1143. $C_{13}H_{16}O_2$ requires M, 204.1150); $\nu_{max}(CHCl_3)/cm^{-1}$ 1762; δ_H 0.83 (1 H, t, *J* 7.0), 0.84 (2 H, t, *J* 7.0), 1.72–1.96 (2 H, m), 2.06–2.24 (2 H, m), 2.79–2.86 (1 H, m), 2.97–3.06 (1 H, m), 3.90 (0.66 H, ddd, *J* 9.0, 9.0 and 4.0), 4.01 (0.33 H, ddd, *J* 9.0, 7.5 and 4.5), 4.07 (0.66 H, ddd, *J* 9.0, 9.0 and 9.0), 4.19 (0.33 H, ddd, *J* 7.0, 7.0 and 7.0) and 7.17–7.35 (5 H, m); δ_C 11.8 (q), 12.1 (q), 23.8 (t), 25.2 (t), 25.6 (t), 26.1 (t), 44.3 (d), 45.0 (d), 46.9 (d), 47.2 (d), 66.2 (t), 66.3 (t), 126.7 (d), 127.9 (d), 128.0 (d), 128.25 (d), 128.34 (d), 128.4 (d), 140.6 (s), 141.7 (s), 178.0 (s) and 178.4 (s); *m/z* 204 (M^+, 8%), 131 (19), 119 (32), 91 (98) and 86 (100).

3-(1-*Phenylbutyl*)*tetrahydrofuran*-2-*one* **7d** [2.0 g, 84% yield as a 2:1 diastereoisomeric mixture‡ from a mixture of **13d** and **14b** (3.0 g, 10.9 mmol)]: *oil*, b.p. 142–145 °C/0.007 mmHg (Found: M^+, 218.1279. $C_{14}H_{18}O_2$ requires M, 218.1307); $\nu_{max}(CHCl_3)/cm^{-1}$ 1762; δ_H 0.87 (1 H, t, *J* 7.0), 0.88 (2 H, t, *J* 7.0), 1.58–2.25 (6 H, m), 2.75–2.84 (1 H, m), 3.08–3.17 (1 H, m), 3.89 (0.66 H, ddd, *J* 9.0, 9.0 and 4.5), 3.99–4.09 (1 H, m), 4.20 (0.33 H, ddd, *J* 7.0, 7.0 and 7.0) and 7.17–7.35 (5 H, m); δ_C 13.66 (q), 13.70 (q), 20.3 (t), 20.6 (t), 25.1 (t), 25.6 (t), 32.9 (t), 35.2 (t), 44.5 (d), 44.7 (d), 45.0 (d), 45.2 (d), 66.18 (t), 66.22 (t), 126.6 (d), 127.8 (d), 127.9 (d), 128.2 (d), 128.37 (d), 128.38 (d), 140.7 (s), 141.9 (s), 178.0 (s) and 178.4 (s); *m/z* 218 (M^+, 7%), 133 (19), 115 (11), 91 (100) and 86 (76).

Preparation of 3-(*Methylsulfanyl*)-3-(α-*substituted Benzyl*)-*tetrahydrofuran*-2-*ones* **9**.—Following a method similar to that used for the preparation of compound **9a**, sulfenylation of the corresponding tetrahydrofuranone **7** was carried out.

3-(*Methylsulfanyl*)-3-(1-*phenylethyl*)*tetrahydrofuran*-2-*one* **9b** [1.8 g, 72% yield as a 1:1 diastereoisomeric mixture‡ from **7b** (2.0 g, 10.5 mmol)]: *oil*. Analytical samples of two diastereoisomers were obtained by means of column chromatography (benzene).

Less polar isomer: *prisms* (from EtOH), m.p. 63–63.5 °C (Found: C, 65.9; H, 6.8%; M^+, 236.0880. $C_{13}H_{16}O_2S$ requires C, 66.07; H. 6.82%; M, 236.0871); $\nu_{max}(CHCl_3)/cm^{-1}$ 1754; δ_H 1.51 (3 H, d, *J* 7.0), 1.91 (1 H, ddd, *J* 13.5, 6.8 and 2.0), 2.24 (3 H, s), 2.52 (1 H, ddd, *J* 13.5, 10.0 and 9.0), 3.48 (1 H, q, *J* 7.0), 3.88 (1 H, ddd, J 9.0, 9.0 and 2.0), 4.23 (1 H, ddd, *J* 10.0, 9.0 and 6.8) and 7.21–7.34 (5 H, m); δ_C 11.8 (q), 15.4 (q), 30.2 (t), 38.9 (d), 53.8 (s), 65.0 (t), 127.2 (d), 128.3 (d), 129.6 (d), 140.1 (s) and 174.5 (s); *m/z* 236 (M^+, 1%), 132 (100), 105 (89) and 91 (5).

More polar isomer: *prisms* (from EtOH), m.p. 100–102 °C (Found: C, 65.8; H, 6.7%; M^+, 236.0875); $\nu_{max}(CHCl_3)/cm^{-1}$ 1754; δ_H 1.36 (3 H, d, *J* 7.0), 1.82 (1 H, ddd, *J* 13.5, 6.0 and 1.0), 2.12 (3 H, s), 2.84 (1 H, ddd, *J* 13.5, 10.8 and 9.0), 3.41 (1 H, q, *J* 7.0), 4.29 (1 H, ddd, *J* 9.0, 9.0 and 1.0), 4.38 (1 H, ddd, *J* 10.8, 9.0 and 6.0), 7.21–7.24 (2 H, m) and 7.26–7.35 (3 H, m); δ_C 11.8 (q), 17.4 (q), 30.7 (t), 40.4 (d), 53.7 (s), 64.9 (t), 127.2 (d), 128.2 (d), 141.4 (s) and 174.7 (s); *m/z* 236 (M^+, 1%), 132 (100), 105 (93) and 91 (6).

3-(*Methylsulfanyl*)-3-(1-*phenylpropyl*)*tetrahydrofuran*-2-*one* **9c** [1.7 g, 73% yield as a 1.1:1 diastereoisomeric mixture‡ from **7c** (1.9 g, 9.3 mmol)]: *oil*. Analytical samples of two diastereoisomers were obtained by means of column chromatography (benzene).

Less polar isomer: *oil*, b.p. 136–138 °C/0.009 mmHg (Found: C, 67.1; H, 7.3%; M^+, 250.1053. $C_{14}H_{18}O_2S$ requires C, 67.16; H, 7.25%; M, 250.1027); $\nu_{max}(CHCl_3)/cm^{-1}$ 1754; δ_H 0.81 (3 H, t, *J* 7.5), 1.67 (1 H, ddq, *J* 15.0, 13.0 and 7.5), 1.90 (1 H, ddd, *J* 13.8, 7.0 and 2.0), 2.21 (3 H, s), 2.44 (1 H, dqd, *J* 15.0, 7.5 and 3.0), 2.61 (1 H, ddd, *J* 13.8, 9.0 and 9.0), 3.12 (1 H, dd, *J* 13.0 and 3.0) 3.91 (1 H, ddd, *J* 9.0, 9.0 and 2.0), 4.23 (1 H, ddd, *J* 9.0, 9.0 and 7.0) and 7.26–7.34 (5 H, m); δ_C 11.8 (q), 12.2 (q), 21.0 (t), 30.7 (t), 47.1 (d), 53.7 (s), 64.9 (t), 127.1 (d), 128.2 (d), 130.3 (d), 137.4 (s) and 174.1 (s); *m/z* 250 (M^+, 0.2%), 132 (100), 119 (21) and 91 (61).

More polar isomer: *oil*, b.p. 134–136 °C/0.009 mmHg (Found: C, 67.0; H, 7.2%; M^+, 250.1049); $\nu_{max}(CHCl_3)/cm^{-1}$ 1755; δ_H 0.79 (3 H, t, *J* 7.2), 1.60 (1 H, dqd, *J* 13.0, 7.2 and 3.0), 1.77 (1 H, ddq, *J* 13.0, 11.2 and 7.2), 1.93 (1 H, dd, *J* 13.5 and 6.3), 2.09

‡ See footnote on p. 1837.

(3 H, s), 2.87 (1 H, ddd, *J* 13.5, 10.5 and 9.0), 3.07 (1 H, dd, *J* 11.2 and 3.0), 4.30 (1 H, dd, *J* 10.5 and 10.5), 4.38 (1 H, ddd, *J* 10.5, 9.0 and 6.3), 7.17–7.21 (2 H, m) and 7.27–7.36 (3 H, m); δ_C 11.5 (q), 12.5 (q), 25.1 (t), 31.1 (t), 48.6 (d), 53.6 (s), 64.8 (t), 127.0 (d), 128.1 (d), 128.6 (d), 139.5 (s) and 174.8 (s); *m*/*z* 250 (M^+, 0.2%), 132 (100), 119 (21) and 91 (60).

3-(*Methylsulfanyl*)-3-(1-*phenylbutyl*)*tetrahydrofuran*-2-*one* **9d** [1.8 g, 74% yield as a 1.5 : 1 diastereoisomeric mixture ‡ from **7d** (2.0 g, 9.2 mmol)]: *oil*, b.p. 141–143 °C/0.006 mmHg (Found: M^+, 264.1200. $C_{15}H_{20}O_2S$ requires M, 264.1184); ν_{max}(CHCl$_3$)/cm^{-1} 1755; δ_H 0.83 (1.8 H, t, *J* 7.0), 0.89 (1.2 H, t, *J* 7.0), 1.04–1.13 (2 H, m), 1.47 (0.6 H, dddd, *J* 13.5, 10.0, 6.0 and 2.5), 1.65–1.80 (1 H, m), 1.87–1.95 (1 H, m), 2.08 (1.8 H, s), 2.22 (1.2 H, s), 2.26–2.34 (0.4 H, m), 2.65 (0.4 H, ddd, *J* 13.5, 9.0 and 9.0), 2.89 (0.6 H, ddd, *J* 13.5, 10.5 and 9.0), 3.18 (0.6 H, dd, *J* 11.5 and 2.5), 3.24 (0.4 H, dd, *J* 13.5 and 3.0), 3.92 (0.4 H, ddd, *J* 9.0, 9.0 and 2.0), 4.24 (0.4 H, ddd, *J* 9.0, 9.0 and 6.8), 4.30 (0.6 H, dd, *J* 9.0 and 9.0), 4.38 (0.6 H, ddd, *J* 10.5, 9.0 and 6.0) and 7.18–7.35 (5 H, m); δ_C 11.5 (q), 11.7 (q), 13.7 (q), 13.8 (q), 20.3 (t), 21.6 (t), 29.9 (t), 30.6 (t), 31.1 (t), 34.3 (t), 44.7 (d), 46.6 (d), 53.5 (s), 53.6 (s), 64.8 (t), 64.9 (t), 127.0 (d), 127.1 (d), 128.1 (d), 128.5 (d), 130.3 (d), 137.6 (s), 139.9 (s), 174.0 (s) and 174.7 (s); *m*/*z* 264 (M^+, 0.2%), 132 (100), 115 (9) and 91 (87).

3-(α-*Cyclohexylphenylmethyl*)-3-(*methylsulfanyl*)*tetrahydrofuran*-2-*one* **9e** [820 mg, 70% yield as practically a single diastereoisomers from **7e** (1.0 g, 3.88 mmol)]. Recrystallisation from ethanol gave a *single diastereoisomer*: *prisms*, m.p. 116–117 °C (Found: C, 70.8; H, 7.8%; M^+, 304.1499. $C_{18}H_{24}O_2S$ requires C, 71.01; H, 7.95%; M, 304.1497); ν_{max}(CHCl$_3$)/cm^{-1} 1755; δ_H 0.78–1.30 (6 H, m), 1.53–1.80 (5 H, m), 1.96 (3 H, s), 2.12 (1 H, ddd, *J* 13.3, 5.5 and 2.0), 2.94 (1 H, ddd, *J* 13.3, 10.0 and 10.0), 3.05 (1 H, d, *J* 9.0), 4.39–4.46 (2 H, m), 7.11–7.16 (2 H, m) and 7.25–7.34 (3 H, m); δ_C 11.7 (q), 26.1 (t), 26.5 (t), 26.7 (t), 31.0 (t), 31.7 (t), 32.8 (t), 41.8 (d), 51.8 (s), 52.6 (d), 64.8 (t), 126.8 (d), 128.2 (d), 141.4 (s) and 175.3 (s); *m*/*z* 304 (M^+, 0.6%), 173 (15), 132 (100) and 91 (40).

3-(2-*Methyl*-1-*phenylpropyl*)-3-(*methylsulfanyl*)*tetrahydrofuran*-2-*one* **9f** [2.15 g, 77% yield as practically a single diastereoisomer from **7f** (2.3 g, 10.5 mmol)]. Recrystallisation from ethanol gave a *single diastereoisomer*): *needles*, m.p. 93–94 °C (Found: C, 68.05; H, 7.5%; M^+, 264.1170. $C_{15}H_{20}O_2S$ requires C, 68.15; H, 7.62%; M, 264.1184); ν_{max}(CHCl$_3$)/cm^{-1} 1754; δ_H 0.72 (3 H, d, *J* 7.0), 0.99 (3 H, d, *J* 7.0), 1.97 (3 H, s), 1.95–2.05 (1 H, m), 2.13 (1 H, ddd, *J* 13.5, 5.0 and 2.8), 2.99 (1 H, ddd, *J* 13.5, 10.0 and 10.0), 3.01 (1 H, d, *J* 9.0), 4.39–4.46 (2 H, m), 7.13–7.16 (2 H, m) and 7.25–7.34 (3 H, m); δ_C 11.7 (q), 21.4 (q), 21.7 (q), 30.8 (t), 32.2 (d), 51.9 (s), 53.2 (d), 64.7 (t), 126.8 (d), 128.2 (d), 128.6 (d), 141.6 (s) and 175.3 (s); *m*/*z* 264 (M^+, 0.4%), 132 (100), 115 (13) and 91 (50).

3-(*Benzhydryl*)-3-(*methylsulfonyl*)*tetrahydrofuran*-2-*one* **9g** [1.38 g, 78% yield from **7g** (1.5 g, 5.95 mmol)]: *needles*, m.p. 129–130 °C (from EtOH) (Found: C, 72.5; H, 6.2%; M^+, 298.1012. $C_{18}H_{18}O_2S$ requires C, 72.45; H, 6.08%; M, 298.1027); ν_{max}(CHCl$_3$)/cm^{-1} 1754; δ_H 2.06 (3 H, s), 2.29 (1 H, ddd, *J* 13.5, 7.0 and 1.8), 2.85 (1 H, ddd, *J* 13.5, 10.5 and 9.0), 4.04 (1 H, ddd, *J* 9.0, 9.0 and 1.8), 4.35 (1 H, ddd, *J* 10.5, 9.0 and 7.0), 4.83 (1 H, s) and 7.15–7.38 (10 H, m); δ_C 11.9 (q), 32.0 (t), 52.3 (d), 52.4 (s), 64.9 (t), 127.0 (d), 128.4 (d), 128.5 (d), 129.7 (d), 130.0 (d), 139.0 (s), 139.2 (s) and 175.0 (s); *m*/*z* 298 (M^+, 2%), 167 (100), 152 (10) and 91 (8).

Preparation of 3-(α-*Substituted Benzyl*)*furan*-2(5H)-*ones* **5**.—Following a method similar to that described for the reaction of compound **9a**, sodium metaperiodate oxidation of the corresponding tetrahydrofuranone **9** was carried out.

3-(1-*Phenylethyl*)*furan*-2(5H)-*one* **5b** [666 mg, 73% yield from **9b** (1.14 g, 4.83 mmol)]: *oil*, b.p. 140–141 °C/2 mmHg (Found: C, 76.6; H, 6.4%; M^+, 188.0820. $C_{12}H_{12}O_2$ requires C, 76.57; H, 6.43%; M, 188.0817); ν_{max}(CHCl$_3$)/cm^{-1} 1756 and 1643; δ_H 1.55 (3 H, d, *J* 7.2), 3.88 (1 H, qdt, *J* 7.2, 1.8 and 1.8), 4.74 (1 H, ddd, *J* 19.0, 1.8 and 1.8), 4.78 (1 H, ddd, *J* 19.0, 1.8 and 1.8), 7.02 (1 H, dt, *J* 1.8 and 1.8) and 7.22–7.36 (5 H, m); δ_C 19.8 (q), 36.6 (d), 70.0 (t), 126.8 (d), 127.3 (d), 128.6 (d), 138.9 (s), 142.6 (s), 144.2 (d) and 173.3 (s); *m*/*z* 188 (M^+, 15%), 143 (100), 129 (34), 115 (17) and 91 (20).

3-(1-*Phenylpropyl*)*furan*-2(5H)-*one* **5c** [572 mg, 79% yield from **9c** (900 mg, 3.6 mmol)]: *oil*, b.p. 121–123 °C/0.008 mmHg (Found: C, 77.1; H, 6.95%; M^+, 202.1007. $C_{13}H_{14}O_2$ requires C, 77.20; H, 6.98%; M, 202.0994); ν_{max}(CHCl$_3$)/cm^{-1} 1753 and 1643; δ_H 0.88 (3 H, t, *J* 7.0), 1.85 (1 H, ddq, *J* 14.0, 9.5 and 7.0), 2.08 (1 H, dqd, *J* 14.0, 7.0 and 6.5), 3.59 (1 H, dddt, *J* 9.5, 6.5, 1.6 and 1.6), 4.74 (1 H, ddd, *J* 18.0, 1.6 and 1.6), 4.78 (1 H, ddd, *J* 18.0, 1.6 and 1.6), 7.08 (1 H, dt, *J* 1.6 and 1.6) and 7.21–7.35 (5 H, m); δ_C 12.2 (q), 27.1 (t), 44.2 (d), 70.0 (t), 126.7 (d), 127.8 (d), 128.5 (d), 137.6 (s), 141.1 (s), 144.2 (d) and 173.5 (s); *m*/*z* 202 (M^+, 23%), 157 (48), 129 (78), 117 (78) and 91 (100).

3-(1-*Phenylbutyl*)*furan*-2(5H)-*one* **5d** [387 mg, 79% yield from **9d** (600 mg, 2.27 mmol)]: *oil*, b.p. 125–128 °C/0.008 mmHg (Found: C, 77.6; H, 7.4%; M^+, 216.1175. $C_{14}H_{16}O_2$ requires C, 77.75; H, 7.46%; M, 216.1150); ν_{max}(CHCl$_3$)/cm^{-1} 1755 and 1644; δ_H 0.90 (3 H, t, *J* 7.0), 1.19–1.33 (2 H, m), 1.82 (1 H, dddd, *J* 13.5, 9.5, 9.5 and 6.0), 2.00 (1 H, dddd, *J* 13.5, 9.5, 6.0 and 6.0), 3.70 (1 H, dddt, *J* 9.5, 6.0, 1.6 and 1.6), 4.73 (1 H, ddd, *J* 18.0, 1.6 and 1.6), 4.78 (1 H, ddd, *J* 18.0, 1.6 and 1.6), 7.08 (1 H, dt, *J* 1.6 and 1.6) and 7.20–7.35 (5 H, m); δ_C 13.7 (q), 20.6 (t), 36.1 (t), 42.1 (d), 69.9 (t), 126.6 (d), 127.7 (d), 128.4 (d), 137.5 (s), 141.3 (s), 144.2 (d) and 173.4 (s); *m*/*z* 216 (M^+, 18%), 173 (39), 129 (100), 117 (55) and 91 (87).

3-(α-*Cyclohexylphenylmethyl*)*furan*-2(5H)-*one* **5e** [396 mg, 75% yield from **9e** (627 mg, 2.06 mmol)]: *leaflets*, m.p. 104–106 °C (from hexane) (Found: C, 79.4; H, 7.7%; M^+, 256.1472. $C_{17}H_{20}O_2$ requires C, 79.65; H, 7.86%; M, 256.1463); ν_{max}(CHCl$_3$)/cm^{-1} 1754 and 1641; δ_H 0.77–0.88 (1 H, m), 0.94–1.04 (1 H, m), 1.10–1.31 (3 H, m), 1.41–1.48 (1 H, m), 1.60–1.80 (4 H, m), 2.05 (1 H, ddddd, *J* 11.0, 11.0, 11.0, 3.0 and 3.0), 3.45 (1 H, br d, *J* 11.0), 4.73 (1 H, dm, *J* 18.5), 4.79 (1 H, dm, *J* 18.5), 7.21–7.23 (1 H, m) and 7.18–7.32 (5 H, m); δ_C 26.1 (t), 26.2 (t), 26.3 (t), 31.4 (t), 31.8 (t), 41.1 (d), 49.4 (d), 70.0 (t), 126.7 (d), 128.4 (d), 128.5 (d), 136.8 (s), 141.2 (s), 144.3 (d) and 173.9 (s); *m*/*z* 256 (M^+, 11%), 174 (66), 129 (100), 115 (7) and 91 (3).

3-(2-*Methyl*-1-*phenylpropyl*)*furan*-2(5H)-*one* **5f** [1.18 g, 72% yield from **9f** (2.0 g, 7.58 mmol)]: *oil*, b.p. 140–141 °C/2 mmHg (Found: C, 77.5; H, 7.4%; M^+, 216.1150. $C_{14}H_{16}O_2$ requires C, 77.75; H, 7.46%; M, 216.1150); ν_{max}(CHCl$_3$)/cm^{-1} 1753 and 1644; δ_H 0.79 (3 H, d, *J* 6.8), 0.99 (3 H, d, *J* 6.8), 2.41 (1 H, dsept, *J* 10.5 and 6.8), 3.38 (1 H, br d, *J* 10.5), 4.73 (1 H, dm, *J* 18.0), 4.79 (1 H, dm, *J* 18.0) 7.23–7.25 (1 H, m) and 7.18–7.31 (5 H, m); δ_C 21.1 (q), 21.4 (q), 31.7 (d), 50.6 (d), 70.0 (t), 126.7 (d), 128.3 (d), 128.5 (d), 137.1 (s), 141.4 (s), 144.2 (d) and 173.8 (s); *m*/*z* 216 (M^+, 8%), 174 (20), 129 (100), 115 (15) and 91 (9).

3-*Benzhydrylfuran*-2(5H)-*one* **5g** [365 mg, 87% yield from **9g** (500 mg, 1.68 mmol)]: *leaflets*, m.p. 134–135 °C (from EtOH) (Found: C, 81.6; H, 5.8%; M^+, 250.1003. $C_{17}H_{14}O_2$ requires C, 81.58; H, 5.64%; M, 250.0994); ν_{max}(CHCl$_3$)/cm^{-1} 1759 and 1650; δ_H 4.84 (2 H, dd, *J* 2.0 and 2.0), 5.19 (1 H, br s), 6.96 (1 H, dt, *J* 2.0 and 2.0) and 7.14–7.34 (10 H, m); δ_C 48.0 (d), 70.2 (t), 127.0 (d), 128.5 (d), 128.7 (d), 137.3 (s), 140.7 (s), 147.5 (d) and 173.0 (s); *m*/*z* 250 (M^+, 31%), 231 (24), 205 (100), 165 (19) and 91 (9).

‡ See footnote on p. 1837.

Photolysis of Compound* **5a** *in Methanol.*—A mixture of compound **5a** (100 mg, 0.57 mmol), 1,4-diazabicyclo-[2.2.2]octane† (DABCO) (40 mg, 0.35 mmol), and methanol (200 cm^3) was irradiated for 23 h. Removal of the solvent left a pale brown oil (160 mg) which, on column chromatography (hexane–diethyl ether, 3:1), gave compound **7a** (20.1 mg, 20%), trans-3-*benzyl*-4-(*hydroxymethyl*)*tetrahydrofuran*-2-*one* **16a** (23.6 mg, 20%), 3,3a,8,8a-*tetrahydro*-1H-*indeno*[1,2-c]-*furan*-1-*one* **6a** (7.7 mg, 8%), 3-*benzyl*-3-(*hydroxymethyl*)-*tetrahydrofuran*-2-*one* **17** (4.4 mg, 4%), and the starting material **5a** (9 mg, 9% recovery). The physical and spectral properties of compound **7a** were completely in accord with those of the specimen obtained by catalytic hydrogenation of compound **8a**.

The 4-(*hydroxymethyl*)*tetrahydrofuranone* **16a**: *oil*, b.p. 120–122 °C/0.008 mmHg (Found: M^+, 206.0951. $C_{12}H_{14}O_3$ requires M, 206.0943); $\nu_{max}(CHCl_3)/cm^{-1}$ 3474 and 1764; δ_H 1.60 (1 H, br, exchangeable with D_2O), 2.47 (1 H, ddddd, *J* 8.1, 8.1, 8.1, 6.5 and 4.5), 2.77 (1 H, ddd, *J* 8.1, 8.1 and 4.8), 2.88 (1 H, dd, *J* 13.9 and 8.1), 3.23 (1 H, dd, *J* 13.9 and 4.8), 3.37 (1 H, dd, *J* 10.5 and 6.5), 3.47 (1 H, dd, *J* 10.5 and 4.5), 4.05 (1 H, dd, *J* 9.0 and 8.1), 4.21 (1 H, dd, *J* 9.0 and 8.1) and 7.17–7.36 (5 H, m); δ_C 35.4 (t), 42.0 (d), 42.9 (d), 62.0 (t), 68.9 (t), 126.9 (d), 128.7 (d), 129.9 (d), 137.8 (s) and 178.7 (s); *m*/*z* 206 (M^+, 48%), 148 (100), 129 (17), 104 (15) and 91 (93).

The tetrahydroindenofuranone **6a**: *prisms* (from hexane–diethyl ether), m.p. 114–116 °C (lit.,[18] 121 °C) (Found: M^+, 174.0657. $C_{11}H_{10}O_2$ requires M, 174.0681); $\nu_{max}(CHCl_3)/cm^{-1}$ 1768; δ_H 3.30–3.44 (3 H, m), 4.08 (1 H, br t-like, *J* 7.0), 4.52 (1 H, dd, *J* 9.5 and 1.0), 4.67 (1 H, dd, *J* 9.5 and 7.0) and 7.22–7.35 (4 H, m); δ_C 35.5 (t), 43.0 (d), 45.8 (d), 72.7 (t), 123.9 (d), 124.9 (d), 128.2 (d), 128.9 (d), 141.6 (s), 141.9 (s) and 180.2 (s); *m*/*z* 174 (M^+, 55%), 129 (78) and 116 (100).

The 3-(*hydroxymethyl*)*tetrahydrofuranone* **17**: *oil*, b.p. 119–120 °C/0.008 mmHg (Found: M^+, 206.0916. $C_{12}H_{14}O_3$ requires M, 206.0943); $\nu_{max}(CHCl_3)/cm^{-1}$ 3480 and 1758; δ_H 2.18 (1 H, ddd, *J* 13.0, 8.0 and 4.0), 2.25 (1 H, ddd, *J* 13.0, 8.0 and 8.0), 2.38 (1 H, br s, exchangeable with D_2O), 2.80 (1 H, d, *J* 13.5), 3.06 (1 H, d, *J* 13.5), 3.55 (1 H, ddd, *J* 8.0, 8.0 and 8.0), 3.64 (1 H, d, *J* 11.0), 3.83 (1 H, d, *J* 11.0), 4.14 (1 H, ddd, *J* 8.0, 8.0 and 4.0) and 7.20–7.35 (5 H, m); δ_C 28.4 (t), 38.9 (t), 50.1 (s), 65.9 (t), 66.9 (t), 127.3 (d), 128.7 (d), 129.9 (d), 135.8 (s) and 181.1 (s); *m*/*z* 206 (M^+, 12%), 188 (15), 175 (68), 115 (20) and 91 (100).

Photolysis of Compound **5b** *in Methanol.*—A mixture of compound **5b** (100 mg, 0.53 mmol), DABCO (40 mg, 0.35 mmol), and methanol (200 cm^3) was irradiated for 19 h to give a pale yellow oil (162 mg) which, on column chromatography (hexane–acetone, 20:1), gave 8-*methyl*-3,3a,8,8a-*tetrahydro*-1H-*indeno*[1,2-c]*furan*-1-*one* **6b** (42.2 mg, 42%), a 1:1 diastereoisomeric mixture‡ of 4-(*hydroxymethyl*)-3-(1-*phenylethyl*)*tetrahydrofuran*-2-*one* **16b** (11.7 mg, 10%), and compound **7b** (4.2 mg, 4%). The physical and spectral properties of compound **7b** were completely in accord with those of the specimen obtained by catalytic hydrogenation of compound **8b**.

The tetrahydroindenofuranone **6b**: *oil*, b.p. 107–109 °C/0.008 mmHg (Found: M^+, 188.0839. $C_{12}H_{12}O_2$ requires M, 188.0837); $\nu_{max}(CHCl_3)/cm^{-1}$ 1763; δ_H 1.35 (3 H, d, *J* 7.5), 3.00 (1 H, dd, *J* 8.0 and 1.2), 3.69 (1 H, br q, *J* 7.5), 4.12 (1 H, br dd, *J* 8.0 and 6.5), 4.48 (1 H, dd, *J* 9.5 and 1.2), 4.66 (1 H, dd, *J* 9.5 and 6.5) and 7.22–7.34 (4 H, m); δ_C 22.8 (q), 43.4 (d), 44.4 (d), 50.9 (d), 72.7 (t), 124.0 (d), 124.2 (d), 127.8 (d), 128.4 (d), 140.9 (s), 147.2 (s) and 180.0 (s); *m*/*z* 188 (M^+, 58%), 143 (100), 129 (48) and 115 (32).

The hydroxymethyltetrahydrofuranone **16b**: *oil*, b.p. 135–137 °C/0.009 mmHg (Found: M^+, 220.1092. $C_{13}H_{16}O_3$ requires M, 220.1099); $\nu_{max}(CHCl_3)/cm^{-1}$ 3440 and 1757; δ_H 1.44 (1.5 H, d, *J* 7.0), 1.49 (1.5 H, d, *J* 7.0), 1.70 (1 H, br s, exchangeable with D_2O), 2.38 (0.5 H, m), 2.54 (0.5 H, m), 2.59 (0.5 H, dd, *J* 7.0 and 4.5). 2.75 (0.5 H, dd, *J* 7.0 and 4.0), 3.26 (0.5 H, dd, *J* 10.5 and 7.0), 3.27–3.33 (0.5 H, m), 3.34 (0.5 H, dd, *J* 10.5 and 5.0), 3.44 (0.5 H, dd, *J* 10.5 and 7.0), 3.43–3.48 (0.5 H, m), 3.50 (0.5 H, dd, *J* 10.5 and 5.0), 3.77 (0.5 H, dd, *J* 9.5 and 7.5), 3.98–4.06 (1.5 H, m) and 7.20–7.38 (5 H, m); δ_C 15.5 (q), 19.3 (q), 38.9 (d), 39.2 (d), 39.8 (d), 40.3 (d), 48.3 (d), 48.7 (d), 63.1 (t), 63.4 (t), 68.8 (t), 69.1 (t), 127.1 (d), 127.2 (d), 127.4 (d), 127.5 (d), 128.7 (d), 142.50 (s), 142.53 (s), 178.0 (s) and 178.4 (s); *m*/*z* 220 (M^+, 22%), 162 (33), 116 (15), 105 (100) and 91 (10).

Photolysis of Compound **5c** *in Methanol.*—A mixture of compound **5c** (100 mg, 0.50 mmol), DABCO (40 mg, 0.35 mmol), and methanol (200 cm^3) was irradiated for 19 h to give a pale yellow oil (160 mg) which, on column chromatography (hexane–acetone, 10:1), gave 8-*ethyl*-3,3a,8,8a-*tetrahydro*-1H-*indeno*[1,2-c]*furan*-1-*one* **6c** (50.3 mg, 50%), a 1:1 diastereoisomeric mixture‡ of 4-(*hydroxymethyl*)-3-(1-*phenylpropyl*)-*tetrahydrofuran*-2-*one* **16c** (11.5 mg, 10%), and compound **7c** (3.1 mg, 3%). The physical and spectral properties of compound **7c** were completely in accord with those of the specimen obtained from compound **14a**.

The tetrahydroindenofuranone **6c**: *oil*, b.p. 128–130 °C/0.008 mmHg (Found: M^+, 202.0993. $C_{13}H_{14}O_2$ requires M, 202.0994); $\nu_{max}(CHCl_3)/cm^{-1}$ 1766; δ_H 0.99 (3 H, t, *J* 7.5), 1.62 (1 H, dqd, *J* 14.0, 7.5 and 7.5), 1.72 (1 H, dqd, *J* 14.0, 7.5 and 6.5), 3.08 (1 H, dd, *J* 8.0 and 1.0), 3.52 (1 H, br dd, *J* 7.5 and 6.5), 4.07 (1 H, br dd, *J* 8.0 and 6.5), 4.49 (1 H, dd, *J* 9.0 and 1.0), 4.65 (1 H, dd, *J* 9.0 and 6.5) and 7.21–7.36 (4 H, m); δ_C 11.4 (q), 29.6 (t), 44.7 (d), 48.6 (d), 50.1 (d), 72.8 (t), 123.9 (d), 124.7 (d), 127.8 (d), 128.0 (d), 141.6 (s), 145.6 (s) and 179.8 (s); *m*/*z* 202 (M^+, 52%), 173 (27), 157 (35), 129 (100) and 115 (20).

The hydroxymethyltetrahydrofuranone **16c**: *oil*, b.p. 153–154 °C/0.009 mmHg (Found: M^+, 234.1277. $C_{14}H_{18}O_3$ requires M, 234.1256); $\nu_{max}(CHCl_3)/cm^{-1}$ 3430 and 1762; δ_H 0.86 (1.5 H, t, *J* 7.0), 0.88 (1.5 H, t, *J* 7.0), 1.43 (0.5 H, br s, exchangeable with D_2O), 1.50 (0.5 H, br s, exchangeable with D_2O), 1.74–1.94 (1 H, m), 2.00–2.16 (1 H, m), 2.36–2.42 (0.5 H, m), 2.51 (0.5 H, m), 2.68 (0.5 H, dd, *J* 6.0 and 4.5), 2.72 (0.5 H, dd, *J* 6.0 and 4.5), 2.99 (0.5 H, ddd, *J* 10.0, 4.5 and 4.5), 3.40 (0.5, ddd, *J* 10.0, 6.0 and 6.0), 3.42–3.56 (2 H, m), 3.71 (0.5 H, dd, *J* 9.0 and 7.0), 3.78 (0.5 H, dd, *J* 9.0 and 8.0), 3.95 (0.5 H, dd, *J* 9.0 and 5.5), 3.97 (0.5 H, dd, *J* 9.0 and 4.0) and 7.19–7.35 (5 H, m); δ_C 12.1 (q), 12.4 (q), 24.2 (t), 25.8 (t), 40.1 (d), 40.5 (d), 47.3 (d), 47.5 (d), 48.1 (d), 63.2 (t), 63.5 (t), 68.8 (t), 127.2 (d), 128.3 (d), 128.7 (d), 128.8 (d), 140.5 (s), 140.8 (s), 177.8 (s) and 178.5 (s); *m*/*z* 234 (M^+, 5%), 128 (15), 116 (73) and 91 (100).

Photolysis of Compound **5d** *in Methanol.*—A mixture of compound **5d** (100 mg, 0.46 mmol), DABCO (40 mg, 0.35 mmol), and methanol (200 cm^3) was irradiated for 19 h to give a pale yellow oil (160 mg) which, on column chromatography (hexane–acetone, 10:1), gave 8-*propyl*-3,3a,8,8a-*tetrahydro*-1H-*indeno*[1,2-c]*furan*-1-*one* **6d** (63.8 mg, 64%), a 1:1 diastereoisomeric mixture‡ of 4-(*hydroxymethyl*)-3-(1-*phenylbutyl*)-*tetrahydrofuran*-2-*one* **16d** (11.0 mg, 10%), and compound **7d** (2.8 mg, 3%). The physical and spectral properties of compound

* All the irradiations except those in a Pyrex test tube were carried out under a stream of dry, oxygen-free nitrogen through a Pyrex filter at 25 °C.

† Although oxygen in the nitrogen gas was supposed to have been washed out by passing the gas through an alkaline solution of pyrogallol, DABCO was added in order to avoid the influence of singlet oxygen (*cf.* ref. 25) which might be generated from any remaining oxygen.

‡ See footnote on p. 1837.

7d were completely in accord with those of the specimen obtained from compound **14b**.

The tetrahydroindenofuranone **6d**: *oil*, b.p. 139–140 °C/0.008 mmHg (Found: M^+, 216.1175. $C_{14}H_{16}O_2$ requires M, 216.1150); $\nu_{max}(CHCl_3)/cm^{-1}$ 1766; δ_H 0.96 (3 H, t, *J* 7.0), 1.36–1.67 (4 H, m), 3.08 (1 H, dd, *J* 8.0 and 1.2), 3.58 (1 H, br dd, *J* 7.5 and 6.5), 4.07 (1 H, br dd, *J* 8.0 and 6.5), 4.47 (1 H, dd, *J* 9.0 and 1.0), 4.65 (1 H, dd, *J* 9.0 and 6.5) and 7.20–7.32 (4 H, m); δ_C 13.9 (q), 20.3 (t), 39.0 (t), 44.6 (d), 48.4 (d), 48.9 (d), 72.7 (t), 123.9 (d), 124.7 (d), 127.7 (d), 128.0 (d), 141.5 (s), 145.9 (s) and 179.8 (s); *m/z* 216 (M^+, 36%), 156 (14), 173 (23), 129 (100) and 115 (16).

The hydroxymethyltetrahydrofuranone **16d**: *oil*, b.p. 156–158 °C/0.009 mmHg (Found: M^+, 248.1418. $C_{15}H_{20}O_3$ requires M, 248.1413); $\nu_{max}(CHCl_3)/cm^{-1}$ 3460 and 1763; δ_H 0.88 (1.5 H, t, *J* 7.0), 0.89 (1.5 H, *J* 7.0), 1.23 (1 H, br s, exchangeable with D_2O), 1.54–2.12 (4 H, m), 2.36–2.42 (0.5 H, m), 2.48–2.54 (0.5 H, m), 2.64 (0.5 H, dd, *J* 6.0 and 4.5), 2.70 (0.5 H, dd, *J* 6.0 and 4.5), 3.08 (0.5 H, ddd, *J* 10.0, 4.5 and 4.5), 3.16 (0.5 H, ddd, *J* 10.0, 6.0 and 6.0), 3.42–3.54 (2 H, m), 3.70 (0.5 H, dd, *J* 9.0 and 7.5), 3.77 (0.5 H, dd, *J* 9.0 and 8.0), 3.95 (0.5 H, dd, *J* 9.0 and 5.5), 3.97 (0.5 H, dd, *J* 9.0 and 4.0) and 7.19–7.38 (5 H, m); δ_C 13.9 (q), 20.5 (t), 20.9 (t), 33.3 (t), 34.8 (t), 40.1 (d), 40.5 (d), 45.2 (d), 46.0 (d), 47.7 (d), 47.9 (d), 63.2 (t), 63.5 (t), 68.9 (t), 127.2 (d), 128.2 (d), 128.7 (d), 128.8 (d), 140.7 (s), 141.0 (s), 178.0 (s) and 178.6 (s); *m/z* 248 (M^+, 4%), 133 (17), 128 (10), 116 (52) and 91 (100).

Photolysis of Compound **5e** *in Methanol*.—A mixture of compound **5e** (100 mg, 0.39 mmol), DABCO (40 mg, 0.35 mmol), and methanol (200 cm^3) was irradiated for 5 h to give a pale yellow solid (161 mg) which, on column chromatography (hexane–acetone, 10:1), gave 8-*cyclohexyl*-3,3a,8,8a-*tetrahydro*-1H-*indeno*[1,2-c]*furan*-1-*one* **6e** (78.2 mg, 78%), 8-*phenylspiro*-*bicyclo*[4.2.0]*octane*-7,3′-*tetrahydrofuran*-2′-*one* **20** (1.5 mg, 1.5%), and compound **7e** (2.1 mg, 2%). Formation of a small amount of 3-(α-*cyclohexylphenylmethyl*)-4-(*hydroxymethyl*)-*tetrahydrofuran*-2-*one* **16e** was detected by GC-MS analysis. The physical and spectral properties of compound **7e** were completely in accord with those of the specimen obtained by catalytic hydrogenation of compound **8e**.

The tetrahydroindenofuranone **6e**: *needles* (from hexane–acetone), m.p. 136–137 °C (Found: C, 79.6; H, 7.7%; M^+, 256.1474. $C_{17}H_{20}O_2$ requires C, 79.65; H, 7.86%; M, 256.1464); $\nu_{max}(CHCl_3)/cm^{-1}$ 1763; δ_H 0.94–1.32 (5 H, m), 1.42–1.48 (1 H, m), 1.60–1.82 (5 H, m), 3.14 (1 H, dd, *J* 8.0 and 1.0), 3.49 (1 H, br d, *J* 5.0), 3.99 (1 H, br dd, *J* 8.0 and 7.0), 4.46 (1 H, dd, *J* 9.5 and 1.0), 4.64 (1 H, dd, *J* 9.5 and 7.0) and 7.20–7.30 (4 H, m); δ_C 26.3 (t), 29.1 (t), 30.9 (t), 43.6 (d), 45.6 (d), 46.7 (d), 54.7 (d), 72.8 (t), 123.7 (d), 125.3 (d), 127.8 (d), 127.9 (d), 142.4 (s), 144.3 (s) and 180.3 (s); *m/z* 256 (M^+, 34%), 196 (26), 174 (71), 129 (100) and 115 (14).

The spirotetrahydrofuranone **20**: *oil*, b.p. 117–118 °C/0.004 mmHg (Found: M^+, 256.1451. $C_{17}H_{20}O_2$ requires M, 256.1463); $\nu_{max}(CHCl_3)/cm^{-1}$ 1758; δ_H 1.34 (1 H, dddd, *J* 11.5, 11.5, 11.5 and 3.5), 1.38–1.52 (3 H, m), 1.64–1.72 (1 H, m), 1.82–1.94 (4 H, m), 1.95 (1 H, dddd, *J* 11.5, 11.5, 11.5 and 3.5), 2.08 (1 H, ddd, *J* 11.5, 11.5 and 3.5), 2.15 (1 H, ddd, *J* 13.5, 8.0 and 5.5), 3.70 (1 H, d, *J* 11.5), 3.82 (1 H, ddd, *J* 9.0, 8.0 and 5.5), 4.03 (1 H, ddd, *J* 9.0, 8.0 and 6.5) and 7.10–7.40 (5 H, m); δ_C 23.9 (t), 25.9 (t), 26.1 (t), 27.0 (t), 30.4 (t), 42.9 (d), 46.1 (d), 52.9 (d), 53.8 (s), 66.2 (t), 127.0 (d), 127.4 (d), 128.6 (d), 138.3 (s) and 179.7 (s); *m/z* 256 (M^+, 49%), 165 (53), 129 (43), 117 (100) and 91 (97).

The hydroxymethyltetrahydrofuranone **16e** (Found: M^+, 288.1697. $C_{18}H_{24}O_3$ requires M, 288.1725); *m/z* 288 (M^+, 5%), 172 (68), 148 (100), 116 (71) and 91 (64).

Photolysis of Compound **5f** *in Methanol*.—A mixture of compound **5f** (100 mg, 0.46 mmol), DABCO (40 mg, 0.35 mmol), and methanol (200 cm^3) was irradiated for 14 h to give a pale yellow solid (145 mg), which, on column chromatography (hexane–acetone, 10:1), gave 8-(*isopropyl*)-3,3a,8,8a-*tetrahydro*-1H-*indeno*[1,2-c]*furan*-1-*one* **6f** (79.8 mg, 80%), a 1:1 diastereoisomeric mixture‡ of 4-(*hydroxymethyl*)-3-(2-*methyl*-1-*phenylpropyl*)*tetrahydrofuran*-2-*one* **16f** (8 mg, 7%), and compound **7f** (1.8 mg, 2%). The physical and spectral properties of compound **7f** were completely in accord with those of the specimen obtained by catalytic hydrogenation of compound **8f**.

The tetrahydroindenofuranone **6f**: *needles* (from hexane–acetone), m.p. 119–119.5 °C (Found: C, 77.6; H, 7.5%; M^+, 216.1158. $C_{14}H_{16}O_2$ requires C, 77.75; H, 7.46%; M, 216.1150); $\nu_{max}(CHCl_3)/cm^{-1}$ 1766; δ_H 0.79 (3 H, d, *J* 7.0), 1.01 (3 H, d, *J* 7.0), 2.05 (1 H, sept d, *J* 7.0 and 4.5), 3.10 (1 H, dd, *J* 8.0 and 1.1), 3.53 (1 H, br d, *J* 4.5), 4.01 (1 H, br dd, *J* 8.0 and 6.5), 4.47 (1 H, dd, *J* 9.0 and 1.0), 4.66 (1 H, dd, *J* 9.0 and 6.5) and 7.20–7.31 (4 H, m); δ_C 18.3 (q), 20.2 (q), 33.3 (d), 45.4 (d), 46.0 (d), 55.2 (d), 72.8 (t), 123.7 (d), 125.0 (d), 127.8 (d), 127.9 (d), 142.4 (s), 144.3 (s) and 180.2 (s); *m/z* 216 (M^+, 25%), 174 (20), 129 (100) and 115 (15).

The hydroxymethyltetrahydrofuranone **16f**: *oil*, b.p. 151–153 °C/0.009 mmHg (Found: M^+, 248.1418. $C_{15}H_{20}O_3$ requires M, 248.1413); $\nu_{max}(CHCl_3)/cm^{-1}$ 3450 and 1762; δ_H 0.69 (1.5 H, d, *J* 6.8), 0.85 (1.5 H, d, *J* 6.8), 1.06 (1.5 H, d, *J* 6.8), 1.20 (1.5 H, d, *J* 6.8), 1.66 (1 H, br s, exchangeable with D_2O), 2.24–2.36 (1 H, m), 2.46–2.54 (1 H, m), 2.62–2.72 (1 H, m), 2.90–3.01 (1 H, m), 3.39 (0.5 H, dd, *J* 9.0 and 8.0), 3.57 (0.5 H, dd, *J* 9.0 and 7.0), 3.61–3.70 (2 H, m), 3.85 (0.5 H, dd, *J* 9.0 and 5.0), 3.94 (0.5 H, dd, *J* 9.0 and 4.0) and 7.18–7.34 (5 H, m); δ_C 20.6 (q), 21.4 (q), 21.6 (q), 22.2 (q), 28.5 (d), 29.2 (d), 39.4 (d), 41.7 (d), 43.7 (d), 45.2 (d), 52.7 (d), 55.4 (d), 63.0 (t), 63.7 (t), 68.5 (t), 69.0 (t), 127.1 (d), 127.2 (d), 128.5 (d), 128.69 (d), 128.74 (d), 129.1 (d), 139.2 (s), 141.1 (s), 177.7 (s) and 179.0 (s); *m/z* 248 (M^+, 5%), 148 (80), 132 (34), 116 (100) and 91 (87).

Photolysis of Compound **5g** *in Methanol*.—A mixture of compound **5g** (100 mg, 0.40 mmol), DABCO (40 mg, 0.35 mmol), and methanol (200 cm^3) was irradiated for 14 h to give a pale yellow solid (161 mg), which, on column chromatography (hexane–acetone, 10:1), gave 8-*phenyl*-3,3a,8,8a-*tetrahydro*-1H-*indeno*[1,2-c]*furan*-1-*one* **6g** (57.5 mg, 58%), exo-1,6-*diphenyl*-3-*oxabicyclo*[3.1.0]*hexan*-2-*one* exo-**18g** (22.8 mg, 23%), the endo-*isomer* endo-**18g** (5.9 mg, 6%), and 3-*benzhydryl*-4-(*hydroxymethyl*)*tetrahydrofuran*-2-*one* **16g** (3.4 mg, 3%). Formation of a small amount of compound **7g** was detected by GC-MS analysis.

The tetrahydroindenofuranone **6g**: *needles* (from EtOH), m.p. 137.5–138.5 °C (Found: C, 81.3; H, 5.8%; M^+, 250.1012. $C_{17}H_{14}O_2$ requires C, 81.58; H, 5.64%; M, 250.0994); $\nu_{max}(CHCl_3)/cm^{-1}$ 1767; δ_H 3.30 (1 H, dd, *J* 8.0 and 1.0), 4.22 (1 H, br dd, *J* 8.0 and 6.8), 4.56 (1 H, dd, *J* 9.0 and 1.0), 4.67 (1 H, dd, *J* 9.0 and 6.8), 4.85 (1 H, br s), 7.05–7.09 (2 H, m) and 7.15–7.43 (7 H, m); δ_C 45.0 (d), 52.6 (d), 54.1 (d), 72.6 (t), 124.0 (d), 125.8 (d), 126.9 (d), 127.2 (d), 128.3 (d), 128.7 (d), 128.8 (d), 142.0 (s), 143.9 (s), 144.5 (s) and 178.9 (s); *m/z* 250 (M^+, 42%), 205 (100), 191 (25), 165 (12) and 115 (9).

exo-*Bicyclic lactone* exo-**18g**: *needles* (from hexane), m.p. 114–115 °C (Found: C, 81.4; H, 5.7%; M^+, 250.0964); $\nu_{max}(CHCl_3)/cm^{-1}$ 1768; δ_H 2.71 (1 H, d, *J* 4.5), 3.09 (1 H, dd, *J* 4.5 and 4.5), 4.50 (1 H, d, *J* 9.2), 4.62 (1 H, dd, *J* 9.2 and 4.5), 6.82–6.86 (2 H, m) and 7.06–7.24 (8 H, m); δ_C 27.4 (d), 35.3 (d), 39.9 (s), 68.3 (t), 126.9 (d), 127.8 (d), 127.9 (d), 128.0 (d), 128.2 (d),

‡ See footnote on p. 1837.

129.7 (d), 130.5 (s), 133.6 (s) and 175.4 (s); *m/z* 250 (M^+, 31%), 220 (33), 205 (29), 191 (35) and 91 (100).

endo-*Bicyclic lactone* endo-**18g**: *needles* (from cyclohexane), m.p. 97–98.5 °C (Found: C, 81.4; H, 5.6%; M^+, 250.0987); $\nu_{max}(CHCl_3)/cm^{-1}$ 1764; δ_H 2.91 (1 H, dd, *J* 8.5 and 5.0), 3.10 (1 H, d, *J* 8.5), 4.18 (1 H, d, *J* 10.0), 4.50 (1 H, dd, *J* 10.0 and 5.0), 7.30–7.44 (8 H, m) and 7.55–7.58 (2 H, m); δ_C 30.2 (d), 33.8 (d), 38.7 (s), 64.6 (t), 127.9 (d), 128.0 (d), 128.6 (d), 128.8 (d), 129.0 (d), 129.3 (d), 132.3 (s), 134.9 (s) and 174.6 (s); *m/z* 250 (M^+, 41%), 220 (35), 205 (45), 191 (35) and 91 (100).

The hydroxymethyltetrahydrofuranone **16g**: *oil*, b.p. 162–164 °C/0.006 mmHg (Found: M^+, 282.1237. $C_{18}H_{18}O_3$ requires M, 282.1256); $\nu_{max}(CHCl_3)/cm^{-1}$ 3450 and 1766; δ_H 1.70 (1 H, br s, exchangeable with D_2O), 2.61 (1 H, ddddd, *J* 7.1, 7.0, 5.1, 4.8 and 4.1), 3.33 (1 H, dd, *J* 6.2 and 4.8), 3.56 (1 H, dd, *J* 10.5 and 7.0), 3.63 (1 H, dd, *J* 10.5 and 5.1), 3.72 (1 H, dd, *J* 9.5 and 7.1), 4.04 (1 H, dd, *J* 9.5 and 4.1), 4.53 (1 H, d, *J* 6.2) and 7.21–7.34 (10 H, m); δ_C 41.1 (d), 46.0 (d), 51.2 (d), 63.1 (t), 68.7 (t), 126.9 (d), 127.2 (d), 128.2 (d), 128.6 (d), 128.66 (d), 128.72 (d), 141.2 (s), 141.4 (s) and 177.9 (s); *m/z* 282 (M^+, 68%), 224 (64), 179 (26), 167 (100) and 152 (49).

Photolysis of Compound **5a** *in Acetone*.—A mixture of compound **5a** (80 mg, 0.46 mmol), DABCO (40 mg, 0.35 mmol), and acetone (200 cm^3) was irradiated for 6 h to give a brown oil (150 mg), which, on column chromatography (hexane–diethyl ether, 2:1), gave 3-*benzyl*-4-(2-*hydroxypropan*-2-*yl*)*tetrahydrofuran*-2-*one* **19a** (56.6 mg, 53%) and compound **7a** (13.5 mg, 17%). The physical and spectral properties of compound **7a** were completely in accord with those of the specimen obtained by catalytic hydrogenation of compound **8a**.

The hydroxypropan-2-*yltetrahydrofuranone* **19a**: *oil*, b.p. 136–139 °C/0.008 mmHg (Found: M^+, 234.1274. $C_{14}H_{18}O_3$ requires M, 234.1256); $\nu_{max}(CHCl_3)/cm^{-1}$ 3450 and 1760; δ_H 1.07 (3 H, s), 1.15 (3 H, s), 1.70 (1 H, br s, exchangeable with D_2O), 2.24 (1 H, ddd, *J* 8.0, 5.0 and 5.0), 2.84 (1 H, ddd, *J* 6.5, 5.0 and 5.0), 3.02 (1 H, dd, *J* 14.5 and 6.5), 3.08 (1 H, dd, *J* 14.5 and 5.0), 4.01 (1 H, dd, *J* 9.5 and 8.0), 4.23 (1 H, dd, *J* 9.5 and 5.0) and 7.18–7.35 (5 H, m); δ_C 27.2 (q), 27.3 (q), 36.6 (t), 43.3 (d), 48.6 (d), 67.9 (t), 70.9 (s), 127.0 (d), 128.7 (d), 129.5 (d), 137.6 (s) and 179.3 (s); *m/z* 234 (M^+, 27%), 171 (26), 148 (66), 131 (38) and 91 (100).

Photolysis of Compound **5b** *in Acetone*.—A mixture of compound **5b** (100 mg, 0.53 mmol), DABCO (40 mg, 0.35 mmol), and acetone (200 cm^3) was irradiated for 11 h to give a brown oil (250 mg), which, on column chromatography (hexane–acetone, 10:1), gave a 1:1 diastereoisomeric mixture‡ of 4-(2-*hydroxypropan*-2-*yl*)-3-(1-*phenylethyl*)*tetrahydrofuran*-2-*one* **19b** (17.8 mg, 14%), compound **7b** (12.3 mg, 12%), and the starting material (12.2 mg, 12% recovery). The physical and spectral properties of compound **7b** were completely in accord with those of the specimen obtained by catalytic hydrogenation of compound **8b**.

The hydroxypropan-2-*yltetrahydrofuranone* **19b**: *oil*, b.p. 132–134 °C/0.007 mmHg (Found: M^+, 248.1411. $C_{15}H_{20}O_3$ requires M, 248.1413); $\nu_{max}(CHCl_3)/cm^{-1}$ 3460 and 1756; δ_H 0.92 (1.5 H, s), 0.99 (1.5 H, s), 1.10 (1.5 H, s), 1.12 (1.5 H, s), 1.46 (1.5 H, d, *J* 7.0), 1.47 (1.5 H, d, *J* 7.0), 1.65 (1 H, br s, exchangeable with D_2O), 2.12 (0.5 H, ddd, *J* 7.0, 2.0 and 2.0), 2.22 (0.5 H, ddd, *J* 8.0, 3.0 and 3.0), 2.62 (0.5 H, dd, *J* 7.0 and 2.0), 2.70 (0.5 H, dd, *J* 4.5 and 3.0), 3.31 (0.5 H, qd, *J* 7.0 and 7.0), 3.33 (0.5 H, qd, *J* 7.0 and 4.5), 3.47 (0.5 H, dd, *J* 10.0 and 7.0), 3.79 (0.5 H, dd, *J* 10.0 and 8.0), 4.18 (0.5 H, dd, *J* 10.0 and 2.0), 4.24 (0.5 H, dd, *J* 10.0 and 3.0) and 7.18–7.36 (5 H, m); δ_C 16.3 (q), 18.9 (q), 26.0 (q), 26.3 (q), 26.8 (q), 27.3 (q), 40.3 (d), 41.4 (d), 47.9 (d), 48.4 (d), 48.9 (d), 49.3 (d), 68.2 (t), 68.6 (t), 71.3 (s), 71.4 (s), 127.18 (d), 127.24 (d), 127.6 (d), 127.7 (d), 128.6 (d), 128.7 (d), 142.1 (s), 142.2 (s), 178.7 (s) and 179.0 (s); *m/z* 248 (M^+, 6%), 230 (12), 162 (36), 105 (100) and 91 (9).

Photolysis of Compound **5e** *in Acetone*.—A mixture of compound **5e** (100 mg, 0.39 mmol), DABCO (40 mg, 0.35 mmol), and acetone (200 cm^3) was irradiated for 11 h to give a brown oil (280 mg), which, on column chromatography (hexane–acetone, 10:1), gave 3-(α-*cyclohexylphenylmethyl*)-4-(2-*hydroxypropan*-2-*yl*)*tetrahydrofuran*-2-*one* **19e** (23.1 mg, 19%) as practically a single diastereoisomeric isomer **20** (10.5 mg, 11%), compound **7e** (9.4 mg, 9%), and the starting material (14.2 mg, 14% recovery). The physical and spectral properties of compound **7e** were completely in accord with those of the specimen obtained by catalytic hydrogenation of compound **8e**.

The hydroxypropan-2-*yltetrahydrofuranone* **19e**: *oil*, b.p. 152–155 °C/0.008 mmHg (Found: M^+, 316.2016. $C_{20}H_{28}O_3$ requires M, 316.2037); $\nu_{max}(CHCl_3)/cm^{-1}$ 3479 and 1758; δ_H 0.78–1.90 (11 H, m), 1.14 (3 H, s), 1.16 (3 H, s), 1.97 (1 H, m), 2.17 (1 H, ddd, *J* 7.0, 1.5 and 1.5), 2.89 (1 H, dd, *J* 8.5 and 6.0), 3.02 (1 H, dd, *J* 6.0 and 1.5), 3.35 (1 H, dd, *J* 9.5 and 7.0), 4.06 (1 H, dd, *J* 9.5 and 1.5) and 7.18–7.30 (5 H, m); δ_C 26.20 (t), 26.26 (t), 26.32 (t), 26.8 (q), 27.1 (q), 37.8 (d), 44.5 (d), 48.9 (d), 52.6 (d), 68.5 (t), 71.5 (s), 127.0 (d), 128.3 (d), 129.4 (d), 139.1 (s) and 179.8 (s); *m/z* 316 (M^+, 1%), 234 (30), 172 (38), 144 (97) and 91 (100).

Photolysis of Compound **5g** *in Acetone*.—A mixture of compound **5g** (100 mg, 0.40 mmol), DABCO (40 mg, 0.35 mmol), and acetone (200 cm^3) was irradiated for 6 h to give a brown oil (275 mg), which, on column chromatography (hexane–acetone, 20:1), gave bicycle *exo*-**18g** (46.8 mg, 47%), its diastereoisomer *endo*-**18g** (17.4 mg, 17%), 3-*benzhydryl*-4-(2-*hydroxypropan*-2-*yl*)*tetrahydrofuran*-2-*one* **19g** (19.2 mg, 15%) as an oil, and the starting material (14.2 mg, 14% recovery). Formation of a small amount of compound **7g** was detected by GC-MS analysis.

The hydroxypropan-2-*yltetrahydrofuranone* **19g**: *oil*, b.p. 154–155 °C/0.005 mmHg (Found: M^+, 310.1567. $C_{20}H_{22}O_3$ requires M, 310.1569); $\nu_{max}(CHCl_3)/cm^{-1}$ 3500 and 1760; δ_H 1.18 (3 H, s), 1.19 (3 H, s), 1.35 (1 H, br s, exchangeable with D_2O), 2.31 (1 H, ddd, *J* 8.0, 2.5 and 2.5), 3.42 (1 H, dd, *J* 8.0 and 2.5), 3.90 (1 H, dd, *J* 10.0 and 8.0), 4.21 (1 H, dd, *J* 10.0 and 2.5), 4.28 (1 H, d, *J* 8.0) and 7.20–7.44 (10 H, m); δ_C 26.7 (q), 27.3 (q), 46.4 (d), 50.3 (d), 53.3 (d), 67.7 (t), 71.6 (s), 127.0 (d), 127.2 (d), 128.4 (d), 128.5 (d), 128.6 (d), 129.0 (d), 140.5 (s), 141.4 (s) and 177.5 (s); *m/z* 310 (M^+, 7%), 292 (6), 224 (24), 167 (100) and 152 (8).

Photolysis of Compound **5f** *in Acetonitrile*.—A mixture of compound **5f** (100 mg, 0.46 mmol), DABCO (40 mg, 0.35 mmol), and acetonitrile (200 cm^3) was irradiated for 12 h. Removal of the solvent resulted in complete recovery of the starting material.

Photolysis of Compound **5f** *in Acetonitrile in the Presence of Acetic Acid*.—A mixture of compound **5f** (100 mg, 0.46 mmol), DABCO (40 mg, 0.35 mmol), acetic acid (20 cm^3), and acetonitrile (200 cm^3) was irradiated for 27 h. Removal of the solvent left a 2:1 mixture‡ of compound **6f** and the starting material (total 125 mg).

Photolysis of Compound **5f** *in Benzene*.—A mixture of compound **5f** (100 mg, 0.46 mmol), DABCO (40 mg, 0.35 mmol), and benzene (200 cm^3) was irradiated for 8 h. Removal of the solvent resulted in complete recovery of the starting material.

‡ See footnote on p. 1837.

Photoisomerisation of Bicycle exo-**18g**.—Under argon, a mixture of bicycle *exo*-**18g** (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 a 10:1 diastereoisomeric mixture‡ of bicycles *exo*-**18g** and *endo*-**18g** (total 10 mg).

Photoisomerisation of Compound endo-**18g**.—Compound *endo*-**18g** (10 mg, 0.04 mmol) was irradiated for 5 h under the same conditions as those described for the photoirradiation of its diastereoisomer *exo*-**18g**, to give a 1:5.5 mixture‡ of *exo*-**18g** and *endo*-**18g** (complete recovery by mass).

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‡ See footnote on p. 1837.

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