Furan-2(3*H*)- and -2(5*H*)-ones. Part 7.[1] Photochemical behaviour of tetrahydro- and hexahydro-isobenzofuran-1-one systems: a mechanistic and exploratory study

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The photoreactivity of two variations of the di-π-methane system involving the tetrahydro- and hexahydro-isobenzofuran structures 10 and 11 have been examined and compared with those of β-apolignans 1. The former, 9-phenyl-1,3,4,5,6,7,8,9-octahydronaphtho[2,3-*c*]furan-1-one 10a and 7-phenyl-1,3,4,7-tetrahydroisobenzofuran-1-one 10b, gave primarily the di-π-methane rearrangement products 18a and 18b, respectively, while the hexahydro substrate, 7-phenyl-1,3,4,5,6,7-hexahydroisobenzofuran-1-one 11, afforded mainly the photoreduced products 21–24. This difference in chemoselectivity is explained in terms of the variant configuration of the phenyl group, an axially orientated one migrating most effectively. A new pathway for the reaction leading to the cyclopropano product 18a or 18b, by way of another cyclopropano derivative 19a or 19b, respectively, is described.

Introduction

It is well known that photoirradiation of molecules having a 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 has been termed the di-π-methane rearrangement and has emerged as one of the most general of the excited-state molecular rearrangement processes.[2]

In a previous paper, we reported the regiospecific di-π-methane rearrangement of β-apolignans **1** into the corresponding tetrahydrocyclopropa[*a*]indenes **2** and showed that the rearrangement is common among β-apolignans irrespective of their ring substituents; we also showed that only the phenyl substituent migrates among the three possible di-π-methane systems found in the β-apolignans **1**.[3] In order to establish the origin of the regioselectivity in the photolysis, we initially investigated the photoreactivity of 3,4-dibenzyl-2,5-dihydrofuran-2-one **3**, a system lacking the stereochemical rigidity of compounds **1**, where reverse selectivity of migration was observed to afford a cyclopropano lactone **4** as the sole rearrangement product.[4] In a further study using the monobenzyl analogues, 3-benzyl-2,5-dihydrofuran-2-ones **5**, 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; in this work only the phenyl substituted substrate **5** (R = Ph) resulted in a di-π-methane rearrangement to afford a cyclopropano lactone **7** (R = Ph) in moderate yield.[5] On the other hand, upon irradiation of the 4-benzyl counterparts, 4-benzyl-2,5-dihydrofuran-2-ones **8**, characteristic acceleration of the di-π-methane rearrangement was observed upon introduction of any alkyl substituents at the 'central methane' carbon to afford the corresponding cyclopropano lactones **9** in good yields.[1,6]

These observations suggested that the stereochemical rigidity of β-apolignans **1** could be responsible for the efficient regioselective photorearrangement leading to compounds **2**. In addition, formation of the cyclopropano lactone **7** (R = Ph) upon irradiation of the phenyl-substituted 3-benzyl system **5** (R = Ph) also implied that the stereochemistry established only upon introduction of the phenyl moiety at the 'central methane' carbon had fulfilled any stereoelectronic requirements for the rearrangement in the aryl-butenolidyl-methane system.

With the aim of gaining further insight into the nature of the regioselective photorearrangement of compounds **1**, we have investigated in the present study the photochemistry of 9-phenyl-1,3,4,5,6,7,8,9-octahydronaphtho[2,3-*c*]furan-1-one **10a**, 7-phenyl-1,3,4,7-tetrahydroisobenzofuran-1-one **10b** and its dihydro derivative, 7-phenyl-1,3,4,5,6,7-hexahydroisobenzofuran-1-one **11**, from a stereochemical point of view. Of these three substrates, the first two, **10a** and **10b**, would have similar stereochemistry to that of the β-apolignans **1** as a result of their 1,4-diene structure, while the last, **11**, would not (Scheme 1).

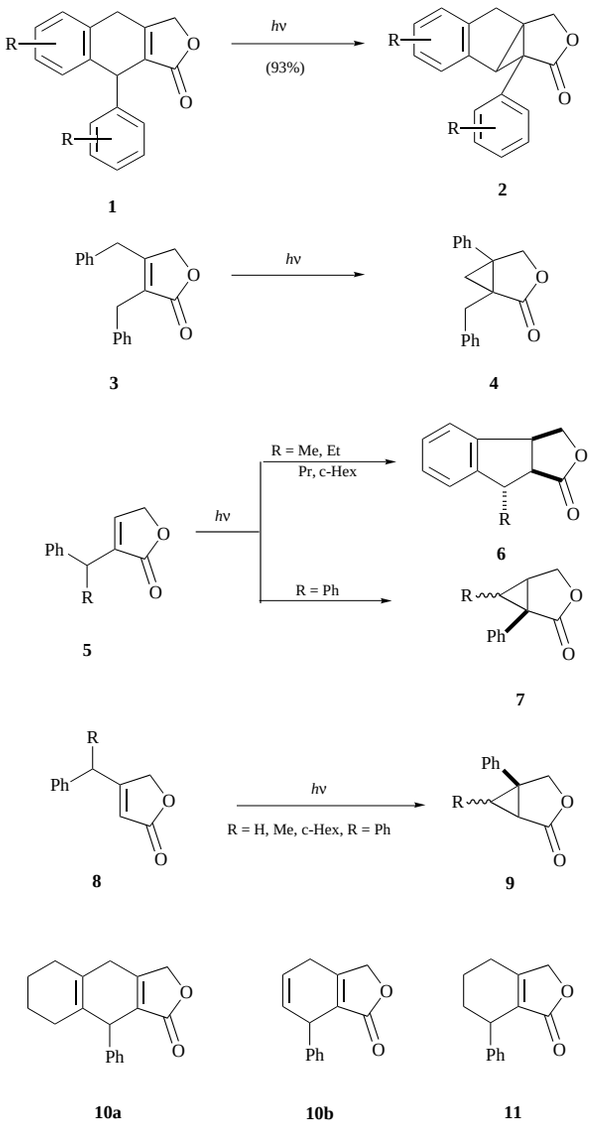
Results

Synthesis of the photochemical substrates 10a, 10b and 11

The Diels–Alder reaction of (*E*)-1-benzylidene-2-methylenecyclohexane **12a**[7] with dimethyl acetylenedicarboxylate (DMAD) gave the desired adduct, dimethyl 1-phenyl-1,4,5,6,7,8-hexahydronaphthalene-2,3-dicarboxylate **13a** (91%). Treatment of this with perchloric acid in formic acid[8] followed by sodium boranuide reduction of the resulting anhydride, 4-phenyl-1,3,4,5,6,7,8,9-octahydronaphtho[2,3-*c*]furan-1,3-dione **14a**, gave a mixture of the desired lactone **10a** and its regioisomer, 4-phenyl-1,3,4,5,6,7,8,9-octahydronaphtho[2,3-*c*]furan-1-one **15a**, in 64 and 11% overall yields, respectively from compound **13a**. The reduction of unsymmetrically substituted succinic anhydride by simple metal hydrides ($NaBH_4$ or $LiAlH_4$) has been reported to occur at the hindered position.[9] Thus, it is interesting to note that in the reduction of the anhydride **14a**, the regioselectivity was reversed to afford primarily compound **10a**, the less hindered site being reduced selectively.

Both lactones **10a** and **15a** displayed similar spectroscopic properties, showing IR absorption at *ca.* 1660, 1698 and 1755 cm^{-1} consistent with the dienone system, and ^1H NMR signals characteristic of homoallylic coupling as a result of the cyclohexa-1,4-diene structure ($J_{4,9}$ 5.0 Hz). In the ^1H NMR spectrum of the minor lactone **15a**, signals arising from the lactonic methylene moiety, which appeared as an AB quartet at δ_H 4.35 and 4.64, shifted upfield in comparison with those of its regioisomer **10a** (δ_H 4.71 and 4.77) due to the anisotropy of the phenyl substituent.

The bicyclic analogue **10b** and its regioisomer, 4-phenyl-1,3,4,7-tetrahydroisobenzofuran-1-one **15b**, were prepared in a



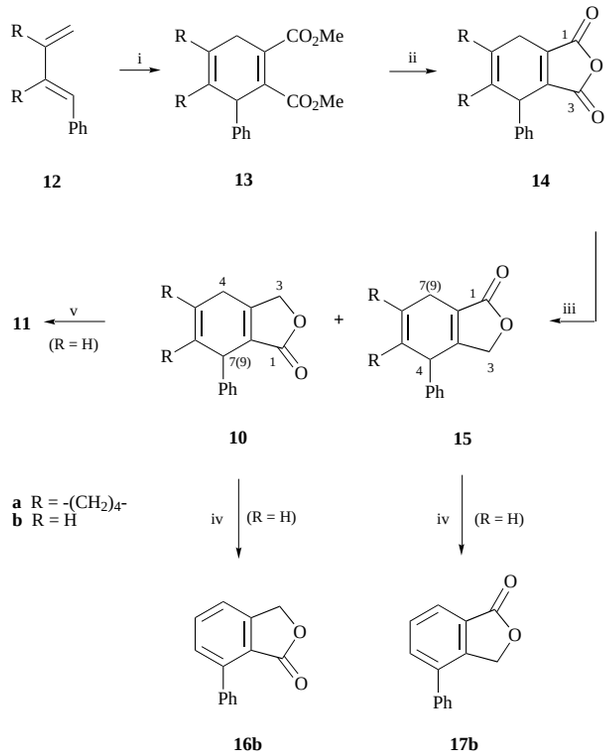
Scheme 1

similar manner starting from (*E*)-1-phenylbuta-1,3-diene **12b**[10] in 57 and 10% overall yields, respectively. Although their spectroscopic properties were well correlated with those of their tricyclic counterparts **10a** and **15a**, the structural confirmation of these two lactones **10b** and **15b** was established by converting them into known compounds, 7-phenyl-1,3-dihydroisobenzofuran-1-one **16b**[11] and 4-phenyl-1,3-dihydroisobenzofuran-1-one **17b**,[11a,12] by dehydrogenation over palladium-on-carbon.

The hexahydroisobenzofuranone **11** was readily prepared by the catalytic hydrogenation of the major bicyclic lactone **10b** over palladium-on-carbon in 88% yield. In its IR spectrum, absorption due to the butenolide system was observed at 1672 and 1750 cm^{-1}, and four triplets at δ_C 18.1, 23.7, 31.7 and 71.1 in its ^{13}C NMR spectrum were consistent with the structure (Scheme 2).

Photolysis of the tricyclic and bicyclic lactones 10a, 10b and 11

Direct irradiation of the tricyclic lactone **10a** in methanol for 15 h afforded primarily the expected di-π-methane rearrangement product, 3a-phenyl-3,3a,3b,4,5,6,7,8-octahydro-1*H*-indeno[2′,1′:1,3]cyclopropa[1,2-*c*]furan-3-one **18a**, in 48% yield. Additionally, formation of two isomeric photorearrangement products, 4a-phenyl-4,4a,6,7,8,9-hexahydro-1*H*,2*H*-cycloprop[1,7a]indeno[1,2-*c*]furan-4-one **19a** and 3c-phenyl-3,3b,3c,4,5,6,7,8-octahydro-1*H*-benzo[1,3]cyclopropa[3,4]cyclopenta[1,2-*c*]furan-3-one **20a** and the dehydrogenated product, 9-phenyl-



Scheme 2 *Reagents and conditions:* i, DMAD, 150 °C or benzene, reflux; ii, $HClO_4$, HCO_2H, reflux; iii, $NaBH_4$; iv, Pd–C, xylene, reflux; v, H_2, Pd–C

1,3,5,6,7,8-hexahydronaphtho[2,3-*c*]furan-1-one **16a**, in 8, 4 and 9% yields, respectively, was also detected.

Upon irradiation of the bicyclic analogue **10b** under the same conditions, phenyl migration to the α-ketonic position also predominated to give a cyclopropano lactone, 3a-phenyl-3,3a,3b,6-tetrahydro-1*H*-cyclopenta[1,3]cyclopropa[1,2-*c*]furan-3-one **18b**, in 43% yield. Its regioisomer, 3a-phenyl-1,1a,3a,4-tetrahydro-6*H*-cyclopropa[1,5]cyclopenta[1,2-*c*]furan-4-one **19b**, and the dehydro derivative **16b** were also produced in 4 and 5% yields, respectively. No rearrangement product of the type **20a** was obtained in this irradiation.

Upon acetone-sensitized irradiation, reactions proceeded more efficiently with both reactants **10a** and **10b**, affording the same respective photoproducts in a shorter reaction time. The results of the irradiations are summarized in Tables 1 and 2 and in Scheme 3.

The minor rearrangement products **19a** and **19b** rearranged into their isomeric cyclopropano lactones **18a** and **18b**, respectively, when irradiated under the acetone-sensitized conditions. Meanwhile, compounds **18a** and **18b** were unaffected by the irradiation, and no reverse transformations leading to **19a** and **19b**, respectively, were detected.

Photolysis of the hexahydroisobenzofuranone **11** proceeded in a completely different manner from that of its dehydro counterpart **10b**. Upon both direct and acetone-sensitized irradiations, photoreduction proceeded predominantly to give four stereoisomeric octahydroisobenzofuranones, 7-phenyl-1,3,3a,4,5,6,7,7a-octahydroisobenzofuran-1-one **21**, **22**, **23** and **24**, in 52–54% combined yields. Formation of a trace amount of a double-bond isomerization product, 7-phenyl-1,3,3a,4,5,6-hexahydroisobenzofuran-1-one **25**, and a di-π-methane rearrangement product, 3a-phenyl-3,3a,3b,4,5,6-hexahydro-1*H*-cyclopenta[1,3]cyclopropa[1,2-*c*]furan-3-one **26**, was also detected. Upon irradiation in methanol, formation of the solvent adducts, 7a-hydroxymethyl-7-phenyl-1,3,3a,4,5,6,7,7a-octahydroisobenzofuran-1-one **27**, **28** and **29**, was detected as additional photoproducts. The product distributions are summarized in Scheme 4.

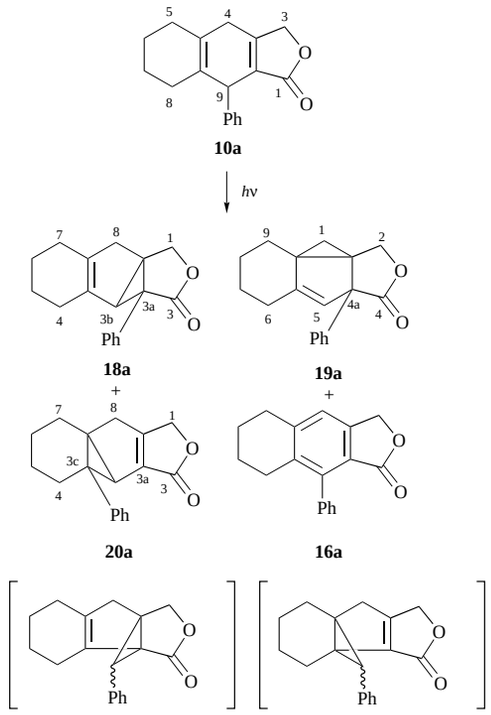
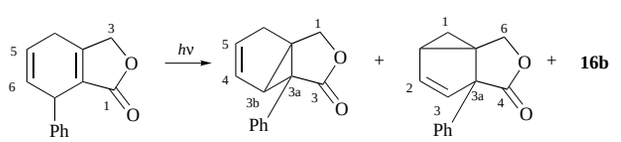


Table 1

Solvent	Reaction time (*t*/h)	Products (isolated yield %)				
		18a	**19a**	**20a**	**16a**	Recovered **10a**
MeOH	15	48	8	4	9	20
Me_2CO	1.5	30	8	18	10	8



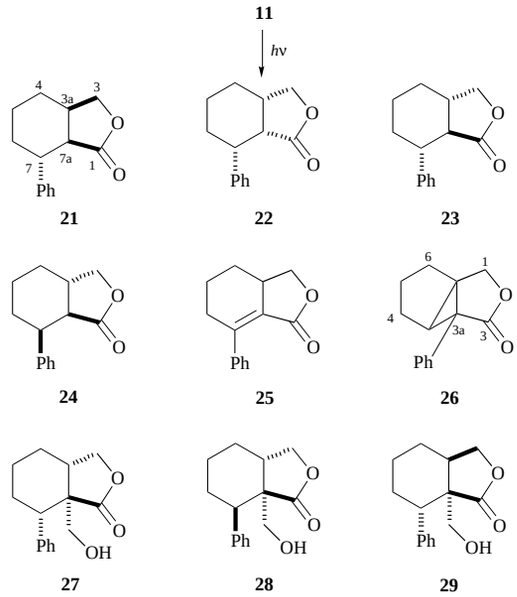
Scheme 3

Table 2

Solvent	Reaction time (*t*/h)	Products (isolated yield %)			
		18b	**19b**	**16b**	Recovered **10b**
MeOH	15	43	4	5	13
Me_2CO	3	48	5	6	4

Structural elucidation of the photoproducts

The di-π-methane rearrangement products **18a**, **19a** and **20a** showed similar spectroscopic properties, and their molecular weights equal to the reactant **10a** implied formation of an additional ring system, introduction of a cyclopropano ring being suggested on the basis of ^{1}H NMR signals in the highfield region. Both compounds **18a** and **19a** showed IR absorption at *ca.* 1760 cm^{-1} arising from the γ-lactone carbonyl, while compound **20a** showed absorption at 1748 cm^{-1} due to its conjugated structure. The adjacent two singlets at δ_C 130.9 and 132.7 due to two olefinic carbons in the ^{13}C NMR spectrum of compound **18a** were assigned to non-conjugated sp^2 carbons, while two separate signals at δ_C 139.4 and 169.9 corresponded to the α- and β-carbons of the enone system in compound **20a**. Signals arising from olefinic carbons in compound **19a** appeared at δ_C 120.9 and 150.7, as a doublet and a singlet, respectively.



Scheme 4

Table 3

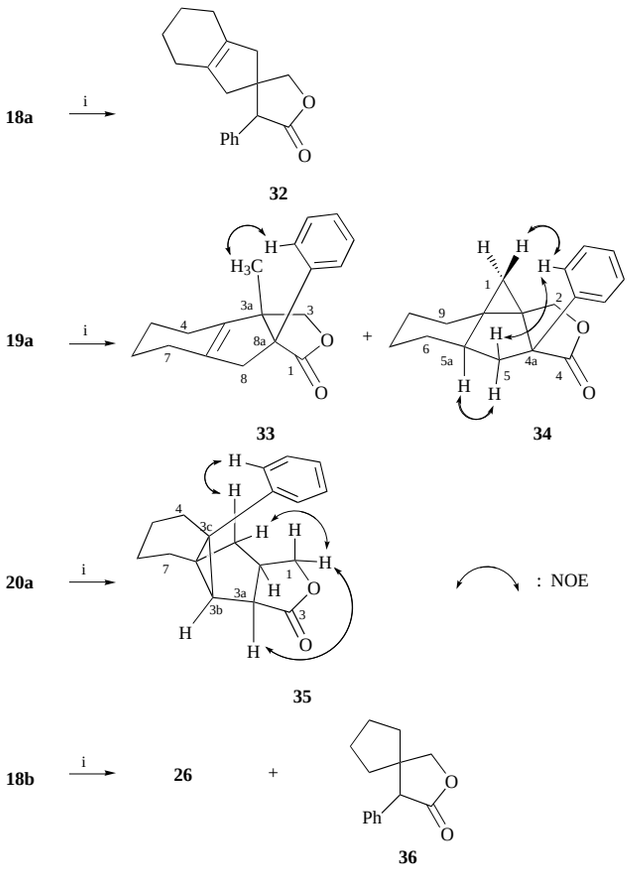
Solvent	Reaction time (*t*/h)	Products (isolated yield %)								
		21/24[a]	**22**	**23**	**25**	**26**	**27**	**28**	**29**	Recovered **11**
MeOH	24	22/5	17	8	2	1	7	6	3	13
Me_2CO	5	21/4	19	10	3	1				11

[a] The product distributions were determined on the basis of 500 MHz ^{1}H NMR spectra.

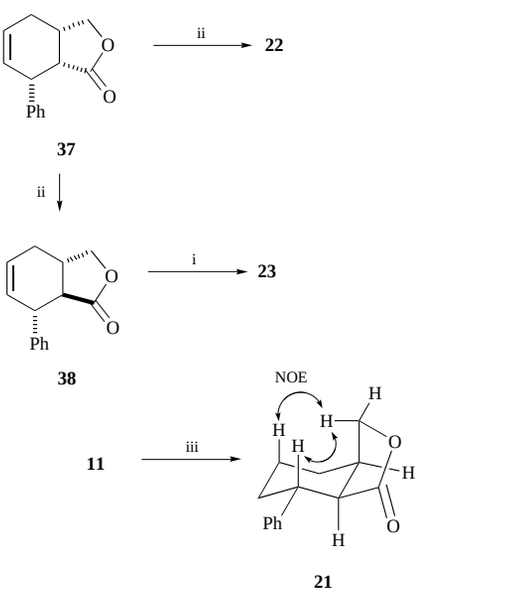
Although this information was consistent with depicted structures **18a**, **19a** and **20a**, formation of other di-π-methane rearrangement products such as compounds **30** or **31**, which might have been produced *via* the alternative di-π-methane system [C(3a)=C(9a)–C(9)–C(8a)=C(4a)] found in compound **10a**, could not be excluded. Therefore, rigorous structural assignments for the products **18a**, **19a** and **20a** were achieved on the basis of degradation studies as shown in Scheme 5.

Thus, hydrogenolysis of the cyclopropano lactone **18a** was carried out over palladium-on-carbon to give 3′-phenylspiro-4,5,6,7-tetrahydroindan-2,4′-tetrahydrofuran-2′-one **32** (84%). A one-proton singlet at δ_H 3.72, a signal typical for the α-methine proton of the phenyl acetate system, and a singlet at δ_C 55.1 corresponding to the spiro carbon were consistent with the depicted structure **32**, a product of cyclopropano ring-cleavage at the benzylic position in compound **18a**. No signal due to benzylic protons, which might have appeared by cleavage of any cyclopropano ring bonds in the suspected product **30**, were detected in the ^{1}H NMR spectrum.

Hydrogenolysis of compound **19a** gave two lactones, 3a-methyl-8a-phenyl-3,3a,4,5,6,7,8,8a-octahydro-1*H*-indeno[1,2-*c*]furan-1-one **33** and 4a-phenyl-4,4a,5,5a,6,7,8,9-octahydro-1*H*,2*H*-cycloprop[1,7a]indeno[1,2-*c*]furan-4-one **34**, in 35 and 26% yields, respectively. The ^{1}H NMR spectrum of the major product **33** displayed a singlet at δ_H 0.73 arising from the terminal methyl, and the relative stereochemistry of the methyl and the phenyl groups was found to be in a *cis* relationship on the basis of differential nuclear Overhauser effect (NOE) experiments. Three singlets at δ_C 135.6, 135.7 and 136.2 represented two non-conjugated olefinic carbons and the *ipso* carbon of the phenyl moiety. In the ^{1}H NMR spectrum of the minor product **34**, signals due to the cyclopropano methylene protons still remained as a pair of doublets at δ_H 0.86 and 1.08, and on the basis of NOE experiments, the cyclopropano ring was



Scheme 5 *Reagents:* i, H_2, Pd–C



Scheme 6 *Reagents and conditions:* i, H_2, Pd–C; ii, NaH, RT, then AcOH; iii, Li, liq. NH_3, −50 °C

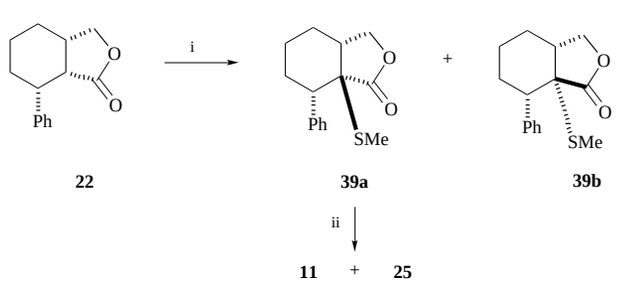
shown to be in a *cis* relationship with the phenyl ring. Signals arising from the methylene protons at C-5 were detected at δ_H 1.71 and 2.42, as a doublet of doublets and a doublet, respectively, and the *trans* relationship of the methine proton at C-5a with the phenyl ring was elucidated by NOE enhancements as shown in Scheme 5.

Finally, catalytic hydrogenation of the lactone **20a** gave 3c-phenyl-3,3a,3b,3c,4,5,6,7,8,8a-decahydro-1*H*-benzo[1,3]cyclopropa[3,4]cyclopenta[1,2-*c*]furan-3-one **35** in 92% yield as the sole product. Its ^{1}H NMR spectrum displayed signals due to α- and β-protons in the lactone moiety at δ_H 3.42 and 3.20, respectively. On the basis of ^{13}C–^{1}H correlation spectroscopy, one of the lactone γ-methylene protons was found to resonate at δ_H 1.85, the highly shielded feature of which was ascribed to the anisotropy of the facing phenyl ring. Between the other lactonic γ-methylene proton, which resonated at δ_H 3.72, and the α-ketonic proton a significant NOE was observed, suggesting that the cyclopropano ring and the γ-lactone moiety was in a *cis* relationship as shown in Scheme 5.

The structure of compounds **18b** and **19b** was assigned by comparison of their spectroscopic properties with those of their homologous analogues **18a** and **19a**, respectively. Formation of fused cyclopenteno rings was evident on the basis of small *cis*-olefinic coupling constants, *i.e. ca.* 5.5 Hz each for $J_{4,5}$ and $J_{2,3}$ in compounds **18b** and **19b**, respectively, in comparison with that of the cyclohexeno moiety ($J_{5,6}$ 10.0 Hz) in the reactant **10b**. Compound **18b** was also exposed to hydrogenolysis to afford compound **26**, which was identical with the di-π-methane rearrangement product obtained in the irradiation of compound **11**, and a degraded spiro compound, 3′-phenylspirocyclopentane-1,4′-tetrahydrofuran-2′-one **36**, the spectral properties of which being correlated with those of the homologous counterpart **32**.

Although the four photoreduced products **21**, **22**, **23** and **24** showed similar NMR spectroscopic properties (Table 4), compounds **21**, **22** and **23** were prepared independently as outlined in Scheme 6 and identified. Thus, by catalytic hydrogenation of the readily available all-*cis* lactone, 7-phenyl-1,3,3a,4,7,7a-hexahydroisobenzofuran-1-one **37**,[11a] all-*cis* octahydroisobenzofuranone **22** was obtained in 85% yield. Treatment of the same reactant **37** with sodium hydride followed by quenching with acetic acid caused isomerization to give an all-*trans* lactone **38**,[11a] which was hydrogenated over palladium-on-carbon to give the corresponding all-*trans* octahydroisobenzofuranone **23** in 85% overall yield from the starting material **37**. Birch reduction of compound **11** afforded the residual octahydroisobenzofuranone **21** in 65% yield, with the observed NOEs shown in Scheme 6 supporting the relative stereochemistry. Spectral properties of the octahydroisobenzofuranones **21**, **22** and **23** thus synthesized were in accord with those of specimens obtained by the photoirradiation of compound **11**.

The double-bond migration product **25** was identical with an authentic sample prepared by sulfenylation of compound **22** followed by oxidative elimination of the methylsulfanyl group of the major sulfide, 7a-methylsulfanyl-7-phenyl-1,3,3a,4,5,6,7,7a-octahydroisobenzofuran-1-one **39a**. The major product **11** (59% yield) of the elimination was identical with the photochemical reactant **11** synthesized by the alternative route shown in Scheme 2.



Scheme 7 *Reagents and conditions:* i, MeSSMe, lithium isopropylcyclohexylamide; ii, $NaIO_4$, then heat

Compounds **27**, **28** and **29** displayed IR absorption at 3579–3430 cm^{-1} arising from hydroxy groups, and their molecular ion peaks at *m*/*z* 246 corresponded to the methanol adduct. Large coupling constants (12.0–13.0 Hz) of signals at δ_H 2.46 and 3.01 arising from two methine protons at C-3a and C-7 in compound **27** indicated them to be in the axial (β) orientation, and significant NOE enhancements were observed between each of

Table 4 ^{1}H and ^{13}C NMR spectra of the perhydroisobenzofuranones **21**, **22**, **23** and **24**

	21			**22**		
Position	δ_H [a]		δ_C [b]	δ_H		δ_C
1			177.7 (s)			174.8 (s)
3	4.10 dd	9.0, 3.5	70.9 (t)	3.91 d	9.0	70.9 (t)
	4.29 dd	9.0, 5.5		4.16 dd	9.0, 4.5	
3a	2.86 m		34.8 (d)	2.59 dddd	12.0, 6.0 × 2, 4.5	37.8 (d)
4ax	1.44 m		25.8 (t)	1.35 dddd	13.5 × 2, 12.0, 3.5	26.9 (t)
eq	1.88 m			1.91 dm	13.5	
5ax	1.44–1.52 m		19.2 (t)	1.43 ddddd	13.5 × 3, 3.5 × 2	24.8 (t)
eq	1.44–1.52 m			1.94–2.01 m		
6ax	1.70–1.80 m		30.6 (t)	1.77 dddm	13.5 × 3	26.5 (t)
eq	1.70–1.80 m			1.94–2.01 m		
7	3.33 ddd	5.5, 5.0 × 2	38.6 (d)	3.02 m		40.1 (d)
7a	2.83 m		44.1 (d)	3.04 m		45.5 (d)
arom.	7.20–7.30 (3H, m)		126.4 (d)	7.19–7.26 (1H, m)		126.2 (d)
	7.31–7.36 (2H, m)		127.6 (d)	7.30–7.33 (4H, m)		127.9 (d)
			128.5 (d)			
			143.9 (s)			142.2 (s)

	23			**24**		
Position	δ_H		δ_C	δ_H		δ_C
1			175.2 (s)			176.4 (s)
3	3.86 dd	11.0, 8.5	71.1 (t)	3.81 dd	11.0, 9.0	72.1 (t)
	4.36 dd	8.5, 6.0		4.37 dd	9.0, 6.5	
3a	2.19 ddddd	13.5, 11.0 × 2, 6.0, 3.0	43.7 (d)	2.46 ddddd	14.0, 12.5, 11.0, 6.5, 3.0	36.2 (d)
4ax	1.34 dddd	12.0 × 2, 11.0, 3.0	27.7 (t)	1.34 dddd	12.5 × 3, 4.5	29.1 (t)
eq	1.94–2.04 m			2.02 dm	12.5	
5ax	1.47 ddddd	12.0 × 3, 3.5 × 2	25.6 (t)	1.72 m		21.3 (t)
eq	1.94–2.04 m			1.80 m		
6ax	1.41 m		36.3 (t)	1.75 m		30.8 (t)
eq	1.94–2.04 m			2.35 dm	12.5	
7	2.72 ddd	11.0 × 2, 3.5	43.9 (d)	3.74 br m		36.4 (d)
7a	2.28 dd	13.5, 11.0	48.3 (d)	2.43 dd	14.0, 4.0	49.3 (d)
arom.	7.20–7.25 (3H, m)		126.5 (d)	7.17–7.28 (3H, m)		126.3 (d)
	7.30–7.34 (2H, m)		127.1 (d)	7.40–7.45 (2H, m)		128.2 (d)
			128.3 (d)			128.9 (d)
			142.6 (s)			140.1 (s)

[a] ^{1}H chemical shift values (δ ppm from $SiMe_4$) are followed by the multiplicity of the signals and the coupling constants (J/Hz). [b] Letters s, d, t in parentheses indicate quaternary, tertiary and secondary carbons, respectively.

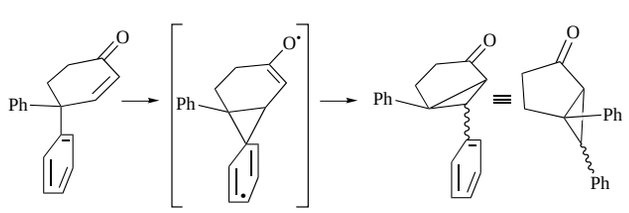
these signals and the axial proton (δ_H 1.52) at C-5. The other NOEs between methylene protons in the hydroxymethyl moiety (δ_H 3.99 and 4.10) and two axial protons at C-4 and C-6 in the cyclohexane ring, which resonated at δ_H 1.58 and 2.13, respectively, supported the depicted stereochemistry. On the other hand, in the NOESY spectrum of compound **28**, both the methine proton at C-3a (δ_H 2.79) and the axial proton at C-5 (δ_H *ca.* 1.96) showed NOEs between aromatic protons at the *ortho* position (δ_H 7.47).

Small couplings of the signal at δ_H 3.16 (J 6.0 and 2.5 Hz), due to the angular proton at C-3a in compound **29**, with methylene protons at C-4 indicated that the proton is in the equatorial (α) configuration. Therefore, the lactonic methylene moiety is axially oriented, and its *cis*-fused ring system was evidenced by appreciable NOEs detected with one of the lactonic methylene protons (δ_H 4.36) between the benzylic methine proton (δ_H 2.92) and also between the axial proton at C-5 (δ_H 1.64).

Discussion

Compounds **10a** and **10b**, when irradiated in methanol or in acetone, gave primarily phenyl-migrated products **18a** and **18b**, displaying a reactivity similar to the β-apolignans **1**, although efficiency and selectivity of the rearrangement decreased. On the other hand, compound **11** afforded mainly photoreduced products **21**–**24**. We first focused on the origin of the different chemoselectivity observed among these three systems **1**, **10** and **11** upon irradiation.

Zimmermann and co-workers have reported in their intensive stereochemical studies on the rearrangement (using diphenylcyclohexenone **40**) that, of the two phenyl groups in the molecule **40**, the axially orientated one had migrated upon irradiation as shown in Scheme 8.[13] Thus, the preferred pendant phenyl migration observed in the irradiation of compounds **1** would depend on the conformation of the phenyl group to migrate, the different photoreactivity among these three systems **1**, **10** and **11** being caused by their variant stereochemical features.



40

Scheme 8

The stereochemistry of cyclohexa-1,4-diene **41**, 1,4-dihydronaphthalene **42**, 9,10-dihydroanthracene **43** and their derivatives had been the subject of considerable interest and, after a long controversy, the planar structure of compound **41** has recently been shown to be correct:[14] introduction of substituents at the C-3 position has been reported to cause only slight conformational changes.[14c] On the other hand, com-

pound **43** has been assumed to exist in the boat conformation in solution, and rapid boat-to-boat inversion was suggested by the failure to observe separate ^{1}H NMR resonances for the pseudoaxial and pseudoequatorial protons at C-9 and C-10, even at low temperatures.[14f] 9-Phenyl-9,10-dihydroanthracene **44** has also been shown to exist as an equilibrium mixture of the two conformers **44a** and **44b** in solution.[14e] On the basis of calculations, the ease of employing the boat conformation among them has been reported as follows: compound **43** > compound **42** > compound **41**, although the planar structure has been assumed to be the most stable.[14d]

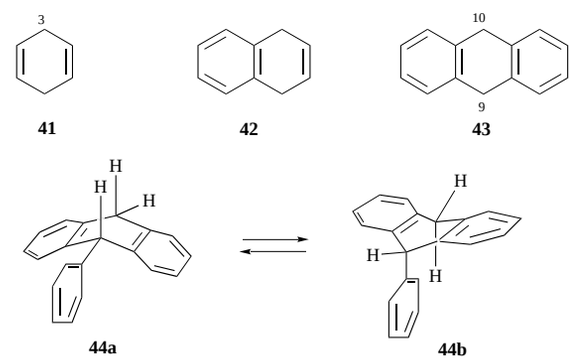
On the basis of this information, it was speculated that compounds **1** and **10** adopted the boat conformation more easily than compound **11** in the photoexcited state. Thus, the efficient chemoselective rearrangement of compounds **1** to compounds **2** upon irradiation would be caused mainly by the pseudoaxial orientation of the phenyl moiety, while in compound **11** the phenyl group would be in the pseudoequatorial direction. The nature of compounds **10a** and **10b** would be intermediate between those of the two systems **1** and **11**.

Upon irradiation of compounds **10a** and **10b**, formation of the unexpected photoproducts **19a** and **19b** was detected, together with an additional phenyl-migrated product **20a** from compound **10a**. The mechanism for the formation of these compounds **19** and **20** is outlined in Scheme 10.

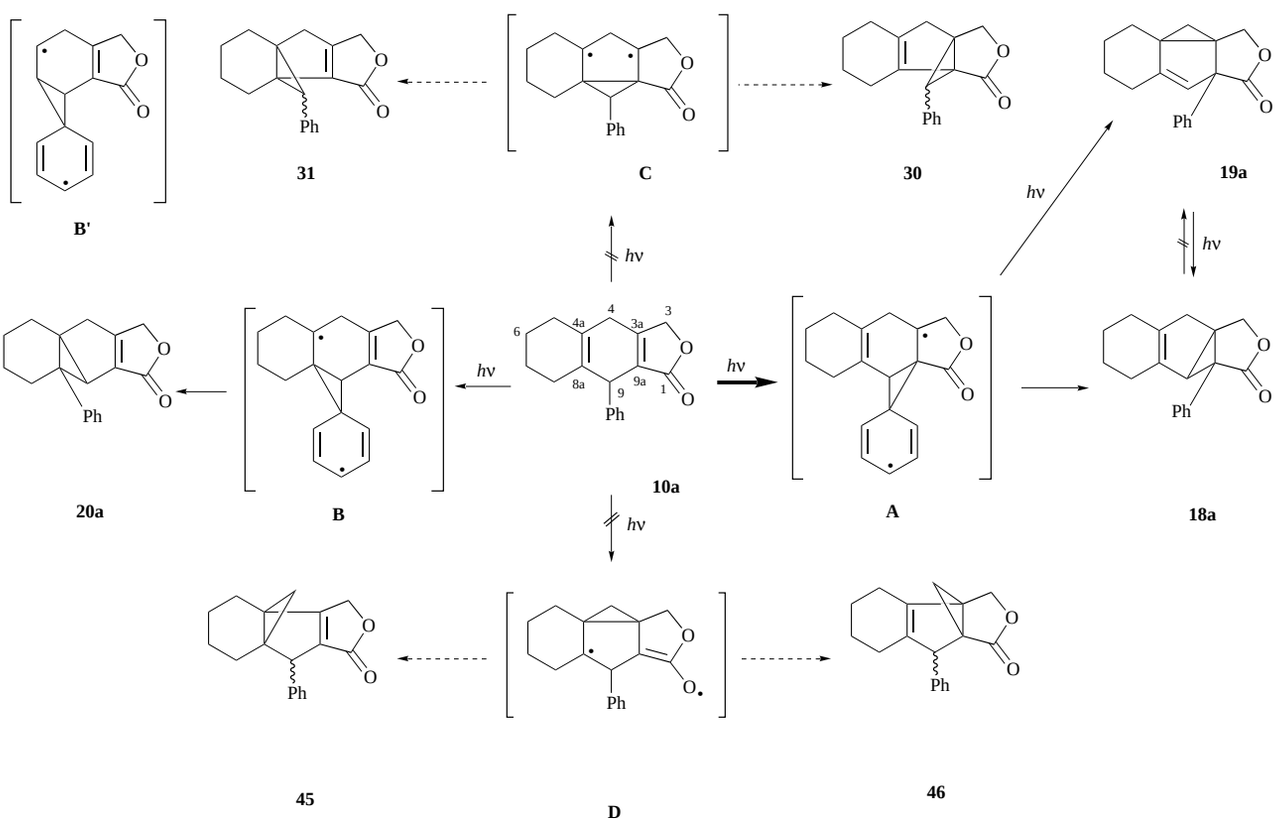
Due to the four di-π-methane systems in the molecule [C(3a)=C(9a)−C(9)–phenyl, C(4a)=C(8a)−C(9)–phenyl, C(3a)=C(9a)−C(9)−C(8a)=C(4a) and C(9a)=C(3a)−C(4)−C(4a)=C(8a)], compound **10a** has the *a priori* possibility of reacting further in four different ways leading to the biradical intermediates **A**, **B**, **C** and **D**. Thus, reactant **10a** has six di-π-methane products **18**, **20**, **30**, **31**, **45** and **46** as possibilities. However, with preferential regioselectivity, the lactone **10a** was transformed into the phenyl-migrated photoproducts **18a** *via* the biradical species of type **A**. The preferable formation of compound **18a** over compound **20a** may be rationalized in terms of the radical-stabilizing effect of the oxygen in the fused lactone moiety, a radical at the β-position to oxygen being reported to be stabilized effectively in such a way.[15] Phenyl migration to the other π-moiety, which was observed upon irradiation of compound **10a**, may be ascribed to the stable nature of the tertiary radical (intermediate **B**) relative to the secondary one (intermediate **B′**). Failure of compounds **30**, **31**, **45** and **46** to be formed may be explained in terms of the difficulty of producing fused bicyclic[3.1.0]hexane systems involving radicals in the skeleton such as intermediates **C** and **D**.

The unexpected minor photoproduct **19a** or **19b** would be produced *via* the intermediate of type **A** through further photorearrangement. It is important to note that whilst compound **19a** is converted into compound **18a** upon irradiation, the reverse does not occur. This observation suggests the presence of an alternative route which leads to the rearrangement product **18a** from compound **10a** besides the well-known pathway directly through the intermediate **A**.

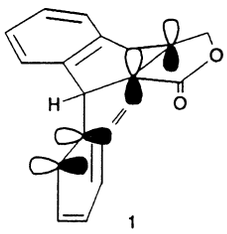
In conclusion, the efficient and regioselective rearrangement observed in the photoirradiation of compounds **1** may now be rationalized mainly in terms of stereochemical rigidity, the conformation with the pseudoaxial phenyl moiety as depicted in



Scheme 9



Scheme 10



1

Fig. 1

Fig. 1, being involved since it fulfils the stereoelectronic requirement for the rearrangement. The rearrangement was found quite sensitive to the described requirements; thus, compound **11** with a pseudoequatorial phenyl moiety gave little of the rearrangement product **26**. Formation of another type of rearrangement product **19** was detected, the alternative pathway for the rearrangement leading to the cyclopropano products **18a** or **18b**, by way of compounds **19a** or **19b**, respectively.

Although our experiments allow certain conclusions to be drawn on the origin of the efficient di-π-methane rearrangement of compounds **1**, a route *via* the planar structure cannot be excluded completely because of the conformational stability of the planar structure with the reactants **1**, **10** and **11**. Further studies on the photoreactivity of the aryl-butenolidyl-methane system from this viewpoint are in progress.

Experimental

Mps were determined on Yanagimoto MP-3S micromelting point apparatus, and mps and bps are uncorrected. IR spectra were measured on a Shimadzu IR-435 grating 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 (δ) and coupling constants (J) are given in ppm and Hz, respectively. All the NMR spectra were taken as $CDCl_3$ solutions with tetramethylsilane as internal standard. Low- and high-resolution mass spectra (electron impact) were recorded on either a Shimadzu QP 1000EX spectrometer or a JEOL JMS-HX 100 spectrometer. UV–Visible spectra were taken on a Hitachi 557 spectrophotometer. Column chromatography was effected over Merck Kieselgel 60 (230–400 mesh) with a pump (FMI model RP). Preparative thin-layer chromatography (PTLC) was performed on Merck Kieselgel 60 F_{254}. All the organic extracts were dried over anhydrous magnesium sulfate prior to evaporation. Light petroleum refers to the fraction distilling in the range 30–70 °C.

Diels–Alder reaction of the dienes 12a and 12b with dimethyl acetylenedicarboxylate (DMAD)

A mixture of (*E*)-1-benzylidene-2-methylenecyclohexane **12a**[7] (11.0 g, 59.8 mmol), dimethyl acetylenedicarboxylate (DMAD, 9.3 g, 65.5 mmol) and benzene (20 cm^3) was heated under reflux for 4 h. After evaporation of the mixture, the residue was triturated with methanol to give an orange solid (19.8 g) which, on recrystallization from methanol, gave *dimethyl* 1-*phenyl*-1,4,5,6,7,8-*hexahydronaphthalene*-2,3-*dicarboxylate* **13a** (17.7 g, 91%) as needles, mp 83–84 °C (Found: C, 73.8; H, 6.9%; M$^+$, 326.1510. $C_{20}H_{22}O_4$ requires C, 73.60; H, 6.79%; *M*, 326.1518); $\nu_{max}(CHCl_3)/cm^{-1}$ 1720 and 1652; δ_H 1.46–1.84 (6H, m), 1.90–2.12 (2H, m), 2.86 (1H, br dd, *J* 23.0 and 5.5), 3.18 (1H, br dd, *J* 23.0 and 7.0), 3.55 (3H, s), 3.76 (3H, s), 4.07 (1H, br t-like, *J* 7.0) and 7.10–7.32 (5H, m); δ_C 22.5 (t), 22.9 (t), 27.5 (t), 29.3 (t), 32.9 (t), 49.5 (d), 51.8 (q), 52.1 (q), 124.6 (s), 126.9 (d), 128.2 (s), 128.38 (d), 128.42 (d), 130.7 (s), 137.5 (s), 141.4 (s), 168.07 (s) and 168.14 (s); *m*/*z* 326 (M$^+$, 13%), 294 (97), 266 (34), 235 (69) and 217 (100).

A benzene-free mixture of (*E*)-1-phenylbuta-1,3-diene **12b**[10] (5.3 g, 40.8 mmol) and DMAD (6.3 g, 44.3 mmol) was heated at 150 °C for 7 h. Work-up in a manner similar to that described above gave an orange solid (10.9 g) which, on recrystallization from methanol, gave *dimethyl* 3-*phenylcyclohexa*-1,4-*diene*-1,2-*dicarboxylate* **13b** (7.4 g, 88%) as prisms, mp 60–61 °C (Found: C, 70.66; H, 6.0%; M$^+$, 272.1027. $C_{16}H_{16}O_4$ requires C, 70.58; H, 5.92%; *M*, 272.1049); $\nu_{max}(CHCl_3)/cm^{-1}$ 1720, 1678 and 1642; δ_H 3.00 (1H, dddd, *J* 23.5, 8.0, 3.5 and 1.5), 3.25 (1H, dddd, *J* 23.5, 8.0, 2.5 and 2.0), 3.53 (3H, s), 3.77 (3H, s), 4.39 (1H, dddd, *J* 8.0, 8.0, 3.5 and 1.5), 5.75 (1H, dddd, *J* 10.5, 3.5, 2.0 and 1.5), 5.83 (1H, dddd, *J* 10.5, 3.5, 2.5 and 1.5) and 7.15–7.34 (5H, m); δ_C 27.3 (t), 44.0 (d), 51.8 (q), 52.1 (q), 121.2 (d), 127.1 (d), 127.4 (d), 128.3 (d), 128.6 (d), 131.0 (s), 136.8 (s), 141.3 (s), 168.0 (s) and 168.1 (s); *m*/*z* 272 (M$^+$, 4%), 240 (100), 181 (54), 163 (42), 153 (46) and 115 (11).

Preparation of the cyclic anhydrides 14a and 14b

A mixture of compound **13a** (8.0 g, 24.5 mmol), formic acid (100 cm^3) and perchloric acid (10 cm^3) was heated under reflux for 2 h. After evaporation of the mixture, the residue was diluted with diethyl ether (150 cm^3) and the mixture was washed successively with aq. sodium hydrogen carbonate and brine, and then evaporated to give a pale brown oil (7.0 g). This, on distillation at reduced pressure, gave 4-*phenyl*-1,3,4,5,6,7,8,9-*octahydronaphtho*[2,3-c]*furan*-1,3-*dione* **14a** (6.0 g, 87%) as an oil, bp 194–196 °C (0.008 mmHg) (Found: M$^+$, 280.1115. $C_{18}H_{16}O_3$ requires *M*, 280.1100); $\nu_{max}(CHCl_3)/cm^{-1}$ 1850, 1772, 1696 and 1658; δ_H 1.56–1.77 (4H, m), 1.80–1.90 (2H, m), 2.07–2.24 (2H, m), 3.04 (1H, br dd, *J* 24.0 and 6.5), 3.16 (1H, br dd, *J* 24.0 and 6.5), 4.17 (1H, br t-like, *J* 6.5) and 7.17–7.36 (5H, m); δ_C 22.5 (t), 22.7 (t), 27.8 (t), 27.9 (t), 30.1 (t), 44.6 (d), 125.4 (s), 127.7 (d), 128.4 (d), 128.7 (s), 128.9 (d), 138.9 (s), 141.2 (s), 144.9 (s), 163.5 (s) and 164.3 (s); *m*/*z* 280 (M$^+$, 100%), 236 (51), 207 (45), 178 (43) and 165 (53).

In a similar manner, compound **13b** (7.0 g, 25.7 mmol) afforded a pale brown solid (5.2 g) which, on recrystallization from hexane, gave 4-*phenyl*-1,3,4,7-*tetrahydroisobenzofuran*-1,3-*dione* **14b** (5.1 g, 88%) as needles, mp 78–80 °C (Found: C, 74.2; H, 4.7%; M$^+$, 226.0660. $C_{14}H_{10}O_3$ requires C, 74.33; H, 4.46%; *M*, 226.0630); $\nu_{max}(CHCl_3)/cm^{-1}$ 1848, 1775, 1687 and 1632; δ_H 3.20 (1H, dddd, *J* 24.0, 7.5, 3.5 and 2.0), 3.27 (1H, dddd, *J* 24.0, 7.5, 3.5 and 3.0), 4.47 (1H, dddd, *J* 7.5, 7.5, 3.5 and 2.0), 5.91 (1H, dddd, *J* 10.0, 3.5, 3.0 and 2.0), 6.02 (1H, dddd, *J* 10.0, 3.5, 3.5 and 2.0) and 7.22–7.37 (5H, m); δ_C 22.5 (t), 39.5 (d), 121.4 (d), 127.5 (d), 127.8 (d), 128.4 (d), 128.9 (d), 138.7 (s), 141.5 (s), 143.9 (s), 163.4 (s) and 164.2 (s); *m*/*z* 226 (M$^+$, 100%), 181 (46) and 152 (58).

Sodium boranuide reduction of the anhydrides 14a and 14b

A solution of the anhydride **14a** (6.0 g, 21.4 mmol) in THF (30 cm^3) was added dropwise to a stirred suspension of sodium boranuide (810 mg, 23.8 mmol) in THF (20 cm^3) at 0 °C, and the resulting mixture was stirred at 0 °C for 1 h. The mixture was then diluted with water (20 cm^3), acidified with 10% hydrochloric acid to pH 2 and stirred at room temperature for 2 h; it was then extracted with diethyl ether. The extract was washed successively with aq. sodium hydrogen carbonate and brine, and evaporated to give a pale yellow solid (6.1 g) which, on recrystallization from ethanol, gave 9-*phenyl*-1,3,4,5,6,7,8,9-*octahydronaphtho*[2,3-c]*furan*-1-*one* **10a** (3.36 g, 59%) as prisms. The mother solution was evaporated to give an orange oil (3.0 g) which, on column chromatography (hexane–diethyl ether, 3:1), gave compound **10a** (805 mg, 14%) and 4-*phenyl*-1,3,4,5,6,7,8,9-*octahydronaphtho*[2,3-c]*furan*-1-*one* **15a** (763 mg, 13%).

Compound **10a**: leaflets, mp 150–151 °C (from EtOH) (Found: C, 81.2; H, 6.9%; M$^+$, 266.1292. $C_{18}H_{18}O_2$ requires C, 81.17; H, 6.81%; *M*, 266.1307); λ_{max}(MeOH)/nm 260 and 267 tailing to *ca.* 290 (ε/dm^3 mol^{-1} cm^{-1} 580 and 315); $\nu_{max}(CHCl_3)$/

cm^{-1} 1755, 1698 and 1659; δ_H 1.54–1.76 (4H, m), 1.80–1.90 (2H, m), 2.04–2.20 (2H, m), 2.89 (1H, br dd, *J* 23.0 and 5.0), 3.11 (1H, br dm, *J* 23.0), 3.99 (1H, br t-like, *J* 5.0), 4.71 (1H, dm, *J* 17.5), 4.77 (1H, br d, *J* 17.5), 7.17–7.23 (3H, m) and 7.24–7.29 (2H, m); δ_C 22.6 (t), 22.8 (t), 28.1 (t), 30.1 (t), 30.7 (t), 44.1 (d), 71.0 (t), 124.6 (s), 126.7 (d), 127.9 (s), 128.3 (d), 129.9 (s), 141.0 (s), 157.3 (s) and 172.3 (s); *m*/*z* 266 (M^+, 100%), 237 (22), 179 (23) and 165 (25).

Compound **15a**: prisms, mp 118–120 °C (from diisopropyl ether) (Found: C, 80.9; H, 6.8%; M^+, 266.1277); λ_{max}(MeOH)/nm 261 and 268 tailing to *ca.* 290 (ε/dm^3 mol^{-1} cm^{-1} 699 and 548; ν_{max}($CHCl_3$)/cm^{-1} 1753, 1698 and 1660; δ_H 1.56–1.84 (6H, m), 2.05–2.20 (2H, m), 2.85 (1H, br dd, *J* 23.0 and 5.0), 2.95 (1H, br dm, *J* 23.0), 3.99 (1H, br t-like, *J* 6.0), 4.35 (1H, dm, *J* 17.0), 4.64 (1H, br d, *J* 17.0), 7.08–7.12 (2H, m) and 7.24–7.35 (3H, m); δ_C 22.7 (t), 22.9 (t), 27.3 (t), 28.0 (t), 30.2 (t), 47.7 (d), 70.8 (t), 123.4 (s), 126.9 (s), 127.3 (s), 127.4 (d), 128.0 (d), 129.0 (d), 140.7 (s), 160.9 (s) and 173.6 (s); *m*/*z* 266 (M^+, 100%), 237 (57), 179 (27) and 165 (28).

In a similar manner, the anhydride **14b** (3.3 g, 14.6 mmol) afforded the corresponding lactones, 7-phenyl-1,3,4,7-tetrahydroisobenzofuran-1-one **10b** (2.26 g, 73%) and 4-phenyl-1,3,4,7-tetrahydroisobenzofuran-1-one **15b** (400 mg, 13%).

Compound **10b**: prisms, mp 98–99 °C (from EtOH) (Found: C, 79.4; H, 5.9%; M^+, 212.0828. $C_{14}H_{12}O_2$ requires C, 79.22; H, 5.70%; *M*, 212.0837); λ_{max}(MeOH)/nm 261 and 267 tailing to *ca.* 300 (ε/dm^3 mol^{-1} cm^{-1} 408 and 266); ν_{max}($CHCl_3$)/cm^{-1} 1754, 1693 and 1637; δ_H 3.07 (1H, ddm, *J* 23.0 and 7.0), 3.18 (1H, ddm, *J* 23.0 and 7.0), 4.28 (1H, br m), 4.74 (1H, dm, *J* 17.5), 4.81 (1H, dm, *J* 17.5), 5.90 (1H, dm, *J* 10.0), 5.93 (1H, dm, *J* 10.0), 7.20–7.26 (3H, m) and 7.28–7.32 (2H, m); δ_C 25.2 (t), 38.8 (d), 71.2 (t), 120.8 (d), 126.6 (s), 126.8 (d), 128.1 (d), 128.4 (d), 129.1 (d), 140.7 (s), 157.7 (s) and 172.3 (s); *m*/*z* 212 (M^+, 100%), 183 (21), 167 (97), 152 (42) and 91 (21).

Compound **15b**: prisms, mp 68.5–69 °C (from hexane–diethyl ether) (Found: C, 79.3; H, 5.8%; M^+, 212.0828); λ_{max}(MeOH)/nm 261 and 268 tailing to *ca.* 300 (ε/dm^3 mol^{-1} cm^{-1} 574 and 368); ν_{max}($CHCl_3$)/cm^{-1} 1753, 1692 and 1636; δ_H 2.98 (1H, dm, *J* 23.0), 3.06 (1H, dm, *J* 23.0), 4.30 (1H, br t-like, *J* 8.0), 4.41 (1H, dm, *J* 17.0), 4.68 (1H, dm, *J* 17.0), 5.82 (1H, dddd, *J* 10.0, 3.0, 2.0 and 2.0), 6.02 (1H, dddd, *J* 10.0, 3.5, 3.5, 2.0), 7.13–7.17 (2H, m) and 7.25–7.37 (3H, m); δ_C 22.0 (t), 42.4 (d), 71.0 (t), 123.5 (d), 123.7 (s), 126.7 (d), 127.7 (d), 127.8 (d), 129.1 (d), 140.5 (s), 159.9 (s) and 173.5 (s); *m*/*z* 212 (M^+, 100%), 183 (20), 167 (55), 152 (29) and 91 (22).

Dehydrogenation of the bicyclic lactones 10b and 15b

A mixture of compound **10b** (30 mg, 0.14 mmol), palladium-on-carbon (15 mg) and xylene (5 cm^3) was heated under reflux for 1 h. The catalyst was filtered off, and the filtrate was evaporated to give a solid (30 mg) which, on recrystallization from ligroin, gave 7-phenyl-1,3-dihydroisobenzofuran-1-one **16b** (27 mg, 91%) as prisms, mp 155–156 °C (lit.,[11a] mp 140–142 °C, lit.,[11b] mp 155–157 °C).

In a similar manner, compound **15b** (30 mg, 0.14 mmol) afforded 4-phenyl-1,3-dihydroisobenzofuran-1-one **17b** (28 mg, 94%) as prisms, mp 119–121 °C (from diisopropyl ether) (lit.,[11a] mp 114–116 °C, lit.,[12] mp 120–121 °C). The spectral properties of both compounds **16b** and **17b** were in accord with those reported.

7-Phenyl-1,3,4,5,6,7-hexahydroisobenzofuran-1-one 11

A suspension of 5% palladium-on-carbon (50 mg) in ethanol (5 cm^3) was pre-equilibrated with hydrogen. To the suspension was added a solution of compound **10b** (400 mg, 1.88 mmol) in ethanol (5 cm^3), and hydrogenation was continued at room temperature and atmospheric pressuric for 1.5 h. The catalyst was filtered off, and the filtrate was evaporated to give a solid (406 mg) which, on recrystallization from diisopropyl ether, gave the *title compound* **11** (354 mg, 88%) as prisms, mp 63–64 °C (Found: C, 78.3; H, 6.65%; M^+, 214.1005. $C_{14}H_{14}O_2$ requires C, 78.48; H, 6.59%; *M*, 214.0994); λ_{max}(MeOH)/nm 258, 266 and 290 (ε/dm^3 mol^{-1} cm^{-1} 424, 276 and 69); ν_{max}($CHCl_3$)/cm^{-1} 1750 and 1672; δ_H 1.70–2.08 (4H, m), 2.37 (1H, br ddd, *J* 18.5, 7.0 and 7.0), 2.47 (1H, br ddd, *J* 18.5, 5.0 and 5.0), 3.77 (1H, br s-like), 4.77 (1H, dm, *J* 17.5), 4.84 (1H, br d, *J* 17.5), 7.09–7.13 (2H, m) and 7.19–7.31 (3H, m); δ_C 18.1 (t), 23.7 (t), 31.7 (t), 36.6 (d), 71.7 (t), 126.4 (d), 127.4 (s), 127.5 (d), 128.3 (d), 142.2 (s), 163.0 (s) and 173.0 (s); *m*/*z* 214 (M^+, 100%), 185 (23), 169 (22), 142 (28), 129 (29) and 91 (21).

Photolysis of compounds 10a, 10b and 11

General procedure. All the irradiations, except those in a Pyrex test tube, were carried out with a solution of the reactant (100 mg) in methanol (200 cm^3) or acetone (200 cm^3) under argon through a Pyrex filter in a water-cooled quartz immersion-well apparatus fitted with an Ishii UV-HT 200 W high-pressure mercury lamp (time and product distribution are given in Tables 1, 2 and 3 in Schemes 3 and 4). Prior to photolysis, solutions were degassed by sonication for 30 min followed by a 30 min argon purge. Products were isolated by column chromatography of the residue left after removal of the solvent using hexane–acetone (30 : 1) as an eluent for compounds **16**, **18**, **19** and **20** and hexane–diethyl ether (4 : 1) for compounds **21**–**29**.

Photolysis of the tricyclic lactone 10a in methanol. Three rearrangement products, 3a-*phenyl*-3,3a,3b,4,5,6,7,8-*octahydro*-1H-*indeno*[2′1′ : 1,3]*cyclopropa*[1,2-c] *furan*-3-*one* **18a**, 4a-*phenyl*-4,4a,6,7,8,9-*hexahydro*-1H,2H-*cycloprop*[1,7a]*indeno*-[1,2-c] *furan*-4-*one* **19a**, 3c-*phenyl*-3,3b,3c,4,5,6,7,8-*octahydro*-1H-*benzo*[1,3]*cyclopropa*[3,4]*cyclopenta*[1,2-c] *furan*-3-*one* **20a** and a dehydrogenated product, 9-*phenyl*-1,3,5,6,7,8-*hexahydronaphtho*[2,3-c] *furan*-1-*one* **16a**, were obtained with a recovery of a small amount of the starting material **10a**.

Compound **18a**: needles, mp 128–130 °C (from EtOH) (Found: C, 81.3; H, 7.0%; M^+, 266.1321. $C_{18}H_{18}O_2$ requires C, 81.17; H, 6.81%; *M*, 266.1307); ν_{max}($CHCl_3$)/cm^{-1} 1759; δ_H 1.08–1.82 (6H, m), 2.03–2.09 (2H, br m), 2.30 (1H, dm, *J* 18.0), 2.39 (1H, br s), 2.67 (1H, br d, *J* 18.0), 4.47 (1H, d, *J* 9.0), 4.57 (1H, d, *J* 9.0), 7.18–7.22 (2H, m) and 7.24–7.33 (3H, m); δ_C 22.2 (t), 22.5 (t), 25.0 (t), 26.0 (t), 35.7 (t), 38.6 (s), 40.6 (s), 41.8 (d), 69.2 (t), 127.8 (d), 128.2 (d), 130.7 (d), 130.9 (s), 132.7 (s), 137.2 (s) and 175.8 (s); *m*/*z* 266 (M^+, 100), 221 (50), 207 (27), 179 (60) and 165 (51).

Compound **19a**: prisms, mp 92–94 °C (from EtOH) (Found: M^+, 266.1336); ν_{max}($CHCl_3$)/cm^{-1} 1763 and 1633; δ_H 0.87 (1H, d, *J* 6.0), 0.90 (1H, d, *J* 6.0), 1.20–1.42 (2H, m), 1.54 (1H, ddddd, *J* 13.0, 13.0, 13.0, 3.5 and 3.5), 1.76 (1H, ddd, *J* 13.0, 13.0 and 3.5), 1.86–1.98 (2H, m), 2.10 (1H, dddd, *J* 14.5, 13.0, 5.0 and 2.5), 2.53 (1H, dm, *J* 14.5), 4.17 (1H, d, *J* 9.0), 4.71 (1H, d, *J* 9.0), 5.43 (1H, d, *J* 2.5) and 7.25–7.37 (5H, m); δ_C 22.3 (t), 24.2 (t), 25.4 (t), 27.4 (t), 28.7 (t), 34.9 (s), 37.5 (s), 63.2 (s), 68.0 (t), 120.9 (d), 126.5 (d), 127.5 (d), 128.8 (d), 137.7 (s), 150.7 (s) and 178.3 (s); *m*/*z* 266 (M^+, 100), 221 (50), 179 (90), 165 (81) and 115 (29).

Compound **20a**: prisms, mp 158–159 °C (from hexane–ethyl acetate) (Found: M^+, 266.1304); ν_{max}($CHCl_3$)/cm^{-1} 1748 and 1651; δ_H 1.32 (1H, m), 1.42–1.60 (3H, m), 1.90 (1H, m), 1.96–2.12 (2H, m), 2.18 (1H, br s), 2.21 (1H, m), 2.49 (1H, br d, *J* 19.0), 2.55 (1H, br d, *J* 19.0), 3.86 (1H, dm, *J* 18.0), 4.51 (1H, dm, *J* 18.0), 7.04–7.15 (3H, m) and 7.20–7.29 (2H, m); δ_C 21.7 (t), 22.5 (t), 28.9 (t), 30.6 (d), 34.9 (t), 37.9 (t), 38.3 (s), 40.3 (s), 68.3 (t), 125.9 (d), 128.3 (d), 129.6 (d), 139.4 (s), 141.8 (s), 169.9 (s) and 170.1 (s); *m*/*z* 266 (M^+, 95), 221 (92), 193 (52), 179 (100), 165 (75), 115 (52) and 91 (85).

Compound **16a**: plates, mp 140–141 °C (from benzene–hexane) (Found: C, 81.6; H, 6.2%; M^+, 264.1173. $C_{18}H_{16}O_2$ requires C, 81.79; H, 6.10%; *M*, 264.1150); ν_{max}($CHCl_3$)/cm^{-1} 1757; δ_H 1.67–1.84 (4H, m), 2.50 (2H, t, *J* 6.5), 2.95 (2H, t, *J* 6.5), 5.20 (2H, s), 7.17–7.22 (2H, m), 7.19 (1H, br s) and 7.37–7.47 (3H, m); δ_C 22.2 (t), 22.8 (t), 27.5 (t), 30.9 (t), 67.9 (t),

120.4 (s), 121.5 (d), 127.5 (d), 128.0 (d), 128.7 (d), 136.0 (s), 137.0 (s), 141.4 (s), 144.0 (s), 144.7 (s) and 169.9 (s); *m*/*z* 264 (M^+, 68), 219 (100), 204 (32), 192 (15), 178 (17) and 165 (16).

Photolysis of the bicyclic lactone 10b in methanol. Two rearrangement products, 3a-*phenyl*-3,3a,3b,6-*tetrahydro*-1H-*cyclopenta*[1,3]*cyclopropa*[1,2-c]*furan*-3-*one* **18b** and 3a-*phenyl*-1,1a,3a,4-*tetrahydro*-6H-*cyclopropa*[1,5]*cyclopenta*[1,2-c]*furan*-4-*one* **19b**, and the dehydrogenated product **16b**, were obtained with recovery of a small amount of the starting material **10b**. Compound **16b** was identical with an authentic specimen obtained by dehydrogenation of the substrate **10b**.

Compound **18b**: prisms, mp 176–178 °C (from hexane–diethyl ether) (Found: C, 79.2; H, 5.8%; M^+, 212.0831. $C_{14}H_{12}O_2$ requires C, 79.22; H, 5.70%; *M*, 212.0838); $\nu_{max}(CHCl_3)/cm^{-1}$ 1762; δ_H 2.46 (1H, dm, *J* 19.0), 2.61 (1H, br s), 2.76 (1H, br d, *J* 19.0), 4.52 (1H, d, *J* 9.5), 4.63 (1H, d, *J* 9.5), 5.44 (1H, ddd, *J* 5.5, 2.0 and 2.0), 5.79 (1H, dm, *J* 5.5), 7.16–7.20 (2H, m) and 7.24–7.34 (3H, m); δ_C 32.8 (t), 39.2 (d), 39.8 (s), 40.7 (s), 69.0 (t), 127.8 (d), 128.3 (d), 128.7 (d), 130.4 (s), 131.6 (d), 132.5 (d) and 175.7 (s); *m*/*z* 212 (M^+, 81), 185 (26), 167 (100), 154 (87) and 115 (23).

Compound **19b**: prisms, mp 90–91 °C (from hexane–acetone) (Found: M^+, 212.0834); $\nu_{max}(CHCl_3)/cm^{-1}$ 1762; δ_H 0.76 (1H, dd, *J* 5.5 and 4.0), 1.23 (1H, dd, *J* 8.5 and 5.5), 2.07 (1H, ddd, *J* 8.5, 4.0 and 2.0), 4.29 (1H, d, *J* 9.0), 4.80 (1H, d, *J* 9.0), 5.85 (1H, d, *J* 5.5), 6.17 (1H, dd, *J* 5.5 and 2.0) and 7.23–7.45 (5H, m); δ_C 16.6 (t), 31.4 (d), 31.6 (s), 63.8 (s), 71.3 (t), 126.5 (d), 127.8 (d), 129.0 (d), 131.4 (d), 136.7 (d), 136.9 (s) and 177.3 (s); *m*/*z* 212 (M^+, 20), 182 (25), 167 (100), 153 (63) and 115 (23).

Photolysis of the tricyclic lactone 10a in acetone. Three rearrangement products **18a**, **19a** and **20a**, and the dehydrogenated product **16a** were obtained together with recovery of a small amount of the starting material **10a**.

Photolysis of the bicyclic lactone 10b in acetone. Two rearrangement products **18b** and **19b**, and the dehydrogenated product **16b** were obtained together with recovery of a small amount of the starting material **10b**.

Photolysis of compound 19a in acetone. A mixture of compound **19a** (5.0 mg, 0.019 mmol) and degassed acetone (1.5 cm^3) in a Pyrex test tube was irradiated for 3 h. Evaporation of the reaction mixture left a pale yellow oil (5.0 mg) which was a 1:1.2 mixture of compound **18a** and the starting material **19a**. Upon irradiation of this mixture for a further 3 h under the same conditions, the ratio of the contents scarcely changed (by ^{1}H NMR spectroscopy).

Photolysis of compound 19b in acetone. Compound **19b** (5.0 mg, 0.024 mmol) was irradiated for 3 h under the same conditions as those described for the irradiation of compound **19a**. Evaporation of the reaction mixture left a pale yellow oil (5.0 mg) which was a 11:1 mixture of compound **18b** and the starting material **19b** (by ^{1}H NMR spectroscopy).

Photolysis of compounds 18a and 18b in acetone. Compounds **18a** and **18b** (5.0 mg, each) were irradiated separately for 3 h under the same conditions as those described for the irradiation of compound **19a**. Evaporation of the reaction mixture gave recovery of the starting material **18a** and **18b**. No evidence for the formation of compounds **19a** and **19b** was detected on the basis of their ^{1}H NMR spectra.

Photolysis of compound 11 in methanol. A 4.4:1 mixture of photoreduced products (3aR*,7R*,7aS*)-7-*phenyl*-1,3,3a,4,5,6,7,7a-*octahydroisobenzofuran*-1-*one* **21** and (3aS*,7S*,7aS*)-*isomer* **24**, two other photoreduced products, (3aS*,7R*,7aR*)-*isomer* **22** and (3aS*,7R*,7aS*)-*isomer* **23**, three solvent adducts, (3aS*,7S*,7aS*)-7a-*hydroxymethyl*-7-*phenyl*-1,3,3a,4,5,6,7,7a-*octahydroisobenzofuran*-1-*one* **27**, (3aS*,7R*,7aS*)-*isomer* **28** and (3aR*,7S*,7aS*)-*isomer* **29** and two rearrangement products, 7-*phenyl*-1,3,3a,4,5,6-*hexahydroisobenzofuran*-1-*one* **25** and 3a-*phenyl*-3,3a,3b,4,5,6-*hexahydro*-1H-*cyclopenta*[1,3]*cyclopropa*[1,2-c]*furan*-3-*one* **26**, were obtained with recovery of a small amount of the starting material **11**. ^{1}H and ^{13}C NMR spectral data for the photoreduced products **21**, **22**, **23** and **24** are listed in Table 4.

A 4.4:1 mixture of r-3a,t-7,c-7a- and r-3a,t-7,t-7a-*perhydroisobenzofuranones* **21** and **24**: oil; $\nu_{max}(CHCl_3)/cm^{-1}$ 1768. The two isomers **21** and **24** were separated by GC–MS; for the major isomer **21** (Found: M^+, 216.1177. $C_{14}H_{16}O_2$ requires *M*, 216.1150); *m*/*z* 216 (M^+, 39), 144 (100), 129 (43), 117 (23) and 91 (47). For the minor isomer **24** (Found: M^+, 216.1139); *m*/*z* 216 (M^+, 56), 144 (46), 129 (70), 117 (62) and 91 (100). The ratio of compounds **21** and **24** in the mixture was determined on the basis of the 500 MHz ^{1}H NMR spectrum.

The *all*-cis-*perhydroisobenzofuranone* **22**: prisms, mp 98–100 °C (from isopropyl ether) (Found: C, 77.5; H, 7.4%; M^+, 216.1177. $C_{14}H_{16}O_2$ requires C, 77.75; H, 7.46%; *M*, 216.1150); $\nu_{max}(CHCl_3)/cm^{-1}$ 1770; *m*/*z* 216 (M^+, 100), 144 (59), 129 (39), 117 (42) and 91 (51).

The *all*-trans-*perhydroisobenzofuranone* **23**: prisms, mp 143–145 °C (from diethyl ether) (Found: C, 77.5; H, 7.6%; M^+, 216.1121); $\nu_{max}(CHCl_3)/cm^{-1}$ 1779; *m*/*z* 216 (M^+, 93), 144 (66), 129 (100), 117 (61) and 91 (83).

The r-3a,c-7,c-7a-*hydroxymethylperhydroisobenzofuranone* **27**: needles, mp 150–152 °C (from hexane–diethyl ether) (Found: M^+, 246.1246. $C_{15}H_{18}O_3$ requires *M*, 246.1255); $\nu_{max}(CHCl_3)/cm^{-1}$ 3551, 3430 and 1774; δ_H 1.17 (1H, dd, *J* 8.0 and 2.0, exchangeable with D_2O), 1.52 (1H, ddddd, *J* 13.0, 13.0, 12.0, 4.0 and 4.0), 1.58 (1H, dddd, *J* 12.0, 12.0, 12.0 and 4.0), 1.77 (1H, dm, *J* 12.0), 1.82 (1H, dm, *J* 13.0), 2.04 (1H, dm, *J* 13.0), 2.13 (1H, dddd, *J* 13.0, 13.0, 12.0 and 4.5), 2.46 (1H, dddd, *J* 12.0, 12.0, 8.0 and 3.0), 3.01 (1H, dd, *J* 13.0 and 4.0), 3.99 (1H, dd, *J* 11.5 and 8.0), 4.10 (1H, dd, *J* 11.5 and 2.0), 4.25 (1H, dd, *J* 8.0 and 8.0), 4.29 (1H, dd, *J* 12.0 and 8.0), 7.25–7.31 (2H, m) and 7.31–7.38 (3H, m); δ_C 21.4 (t), 26.0 (t), 27.8 (t), 47.4 (d), 48.0 (d), 49.5 (s), 58.6 (t), 69.4 (t), 127.4 (d), 128.1 (d), 129.3 (d), 140.5 (s) and 177.1 (s); *m*/*z* 246 (M^+, 10), 229 (17), 216 (88), 144 (57), 129 (64), 117 (68) and 91 (100).

The r-3a,t-7,c-7a-*hydroxymethylperhydroisobenzofuranone* **28**: needles, mp 141–142 °C (from hexane–diethyl ether) (Found: M^+, 246.1246); $\nu_{max}(CHCl_3)/cm^{-1}$ 3544, 3431 and 1762; δ_H 1.23–1.28 (1H, br s, exchangeable with D_2O), 1.65 (1H, m), 1.84 (1H, dm, *J* 13.0), 1.92–2.04 (3H, m), 2.16 (1H, dddd, *J* 15.0, 10.5, 7.0 and 6.0), 2.79 (1H, dddd, *J* 13.0, 12.0, 8.0 and 3.5), 3.67 (1H, br d, *J* 6.0), 4.03 (1H, d, *J* 12.0), 4.09 (1H, dd, *J* 12.0 and 8.0), 4.12 (1H, d, *J* 12.0), 4.23 (1H, dd, *J* 8.0 and 8.0), 7.18–7.31 (3H, m) and 7.43–7.51 (2H, m); δ_C 21.1 (t), 22.1 (t), 25.3 (t), 37.7 (d), 39.2 (d), 51.3 (s), 69.0 (t), 70.5 (t), 126.6 (d), 128.0 (d), 129.9 (d), 141.4 (s) and 178.3 (s); *m*/*z* 246 (M^+, 0.6), 228 (4), 215 (97), 144 (100), 129 (63), 117 (54) and 91 (90).

The r-3a,t-7,t-7a-*hydroxymethylperhydroisobenzofuranone* **29**: needles, mp 158–160 °C (from hexane–diethyl ether) (Found: M^+, 246.1244); $\nu_{max}(CHCl_3)/cm^{-1}$ 3579, 3467 and 1761; δ_H 1.44 (1H, dd, *J* 7.0 and 3.5, exchangeable with D_2O), 1.64 (1H, ddddd, *J* 12.5, 12.5, 12.5, 3.5 and 3.5). 1.72 (1H, dm, *J* 12.5), 1.76–1.87 (3H, m), 1.90 (1H, dddd, *J* 12.5, 12.5, 12.5 and 2.5), 2.92 (1H, dd, *J* 12.5 and 3.5), 3.16 (1H, dddd, *J* 11.0, 8.5, 6.0 and 2.5), 3.65 (1H, dd, *J* 11.5 and 3.5), 3.71 (1H, dd, *J* 11.5 and 7.0), 4.32 (1H, dd, *J* 8.5 and 8.5), 4.36 (1H, dd, *J* 11.0 and 8.5), 7.05–7.09 (2H, m) and 7.25–7.34 (3H, m); δ_C 21.3 (t), 21.4 (t), 27.4 (t), 34.9 (d), 42.6 (d), 50.5 (s), 59.5 (t), 67.4 (t), 127.2 (d), 127.9 (d), 129.0 (d), 139.3 (s) and 178.4 (s); *m*/*z* 246 (M^+, 4), 228 (66), 215 (52), 144 (33), 130 (65), 117 (67) and 91 (100).

The *hexahydroisobenzofuranone* **25**: prisms, mp 90–91 °C (from diisopropyl ether) (Found: M^+, 214.1010. $C_{14}H_{14}O_2$ requires *M*, 214.0994); $\nu_{max}(CHCl_3)/cm^{-1}$ 1752 and 1660; δ_H 1.30 (1H, dddd, *J* 13.5, 12.0, 11.0 and 3.0), 1.72 (1H, m), 2.06 (1H, dm, *J* 12.0), 2.13 (1H, dm, *J* 12.0), 2.49 (1H, dddd, *J* 20.0, 11.0, 6.5 and 4.5), 2.57 (1H, dddd, *J* 20.0, 7.0, 3.0 and 2.0), 3.10 (1H, m), 3.81 (1H, dd, *J* 10.0 and 8.5), 4.54 (1H, dd, *J* 8.5 and 8.5) and 7.25–7.38 (5H, m); δ_C 21.7 (t), 25.2 (t), 32.6 (t), 38.3 (d), 71.1 (t), 122.9 (s), 127.4 (d), 127.7 (d), 128.1 (d), 138.2 (s), 150.0

(s) and 168.7 (s); *m*/*z* 214 (M^+, 100), 184 (17), 170 (41), 155 (26), 142 (28), 128 (45) and 115 (30).

The hexahydrocyclopentacyclopropafuranone **26**: needles, mp 92–93 °C (from cyclohexane) (Found: C, 78.5; H, 6.6%; M^+, 214.0985. $C_{14}H_{14}O_2$ requires C, 78.48; H, 6.59%; *M*, 214.0994); $\nu_{max}(CHCl_3)/cm^{-1}$ 1758; δ_H 0.39 (1H, ddddd, *J* 13.0, 11.0, 11.0, 9.0 and 9.0), 1.47 (1H, dddm, *J* 13.0, 9.0 and 9.0), 1.82 (1H, dd, *J* 14.0 and 9.0), 1.87 (1H, d, *J* 5.0), 1.96–2.10 (3H, m), 4.42 (1H, d, *J* 9.0), 4.50 (1H, br d, *J* 9.0), 7.26–7.30 (2H, m) and 7.31–7.40 (3H, m); δ_C 21.8 (t), 25.7 (t), 25.9 (t), 33.3 (d), 38.7 (s), 43.5 (s), 69.6 (t), 128.0 (d), 128.8 (d), 129.8 (d), 131.5 (s) and 176.4 (s); *m*/*z* 214 (M^+, 100), 184 (54), 156 (34), 141 (47), 128 (32), 115 (35) and 91 (27).

Photolysis of compound 11 in acetone. A 5.3:1 mixture of the photoreduced products **21** and **24**, and two other photoreduced products **22** and **23**, and two rearrangement products **25** and **26** were obtained together with recovery of a small amount of the starting material **11**.

Catalytic hydrogenation of compounds 18a, 18b, 19a and 20. Following the method similar to that used for the preparation of compound **11**, compound **18a** (30.0 mg, 0.11 mmol) was hydrogenated, and worked up to give a solid (30.0 mg) which, on recrystallization from ethanol, gave 3′-*phenylspiro*-4,5,6,7-*tetrahydroindan*-2,4′-*tetrahydrofuran*-2′-*one* **32** (25.5 mg, 84%) as colourless prisms, mp 99–100 °C (Found: M^+, 268.1444. $C_{18}H_{20}O_2$ requires *M*, 268.1463); $\nu_{max}(CHCl_3)/cm^{-1}$ 1765; δ_H 1.38–1.60 (5H, m), 1.70–1.93 (3H, m), 1.96 (1H, br d, *J* 16.0), 2.17 (1H, br d, *J* 16.0), 2.38 (1H, br d, *J* 16.0), 2.52 (1H, br d, *J* 16.0), 3.72 (1H, s), 4.18 (1H, d, *J* 8.5), 4.27 (1H, d, *J* 8.5), 7.14–7.19 (2H, m) and 7.28–7.38 (3H, m); δ_C 22.6 (t), 22.7 (t), 25.3 (t), 25.4 (t), 41.5 (t), 46.0 (t), 55.1 (s), 55.7 (d), 78.6 (t), 127.5 (d), 128.5 (d), 129.4 (d), 132.0 (s), 133.0 (s), 133.9 (s) and 177.1 (s); *m*/*z* 268 (M^+, 17), 133 (100), 118 (16), 105 (12) and 91 (68).

In a similar manner, compound **19a** (30.3 mg, 0.11 mmol) afforded quantitatively an oil which, on PTLC (hexane–acetone, 50:1), gave (3aS*,8aS*)-3a-*methyl*-8a-*phenyl*-3,3a,4,5,6,7,8,8a-*octahydro*-1H-*indeno*[1,2-c]*furan*-1-*one* **33** (10.7 mg, 35%) and (1aS*,4aS*,5aR*,9aS*)-4a-*phenyl*-4,4a,5,5a,6,7,8,9-*octahydro*-1H,2H-*cycloprop*[1,7a]*indeno*[1,2-*c*]-*furan*-4-*one* **34** (7.9 mg, 26%).

Compound **33**: oil, bp 147–149 °C/0.007 mmHg (decomp.) (Found: M^+, 268.1449. $C_{18}H_{20}O_2$ requires *M*, 268.1463); $\nu_{max}(CHCl_3)/cm^{-1}$ 1765; δ_H 0.73 (3H, s), 1.60–1.71 (4H, m), 1.88 (1H, br d, *J* 17.5), 1.96 (1H, br dm, *J* 17.5), 2.02 (1H, br dm, *J* 17.5), 2.06 (1H, br d, *J* 17.5), 2.95 (1H, br d, *J* 16.5), 3.08 (1H, br dm, *J* 16.5), 3.87 (1H, d, *J* 9.0), 4.31 (1H, d, *J* 9.0), 7.18–7.23 (2H, m) and 7.26–7.39 (3H, m); δ_C 17.9 (q), 21.3 (t), 22.60 (t), 22.63 (t), 25.6 (t), 43.5 (t), 58.0 (s), 61.7 (s), 72.2 (t), 127.40 (d), 127.43 (d), 128.7 (d), 135.6 (s), 135.8 (s), 136.2 (s) and 182.9 (s); *m*/*z* 268 (M^+, 64), 233 (100), 210 (43), 195 (32), 181 (45) and 167 (42).

Compound **34**: prisms, mp 132.5–134.5 °C (from EtOH) (Found: M^+, 268.1441); $\nu_{max}(CHCl_3)/cm^{-1}$ 1768; δ_H 0.86 (1H, d, *J* 6.0), 1.06 (1H, dddd, *J* 13.0, 13.0, 13.0 and 3.0), 1.08 (1H, d, *J* 6.0), 1.10–1.28 (3H, m), 1.67–1.74 [3H, m, including one-proton doublet of doublets at δ_H 1.71 (*J* 14.0 and 7.0)], 1.80 (1H, dm, *J* 13.0), 1.95 (1H, ddd, *J* 15.0, 13.0 and 4.0), 2.10 (1H, ddd, *J* 13.0, 7.0 and 7.0), 2.42 (1H, d, *J* 14.0), 4.18 (1H, d, *J* 9.0), 4.67 (1H, d, *J* 9.0), 7.23–7.36 (3H, m) and 7.48–7.52 (2H, m); δ_C 16.9 (t), 25.06 (t), 25.11 (t), 29.2 (t), 32.9 (t), 33.2 (s), 38.3 (s), 40.1 (d), 41.3 (t), 57.3 (s), 67.5 (t), 126.7 (d), 127.4 (d), 128.7 (d), 138.8 (s) and 179.9 (s); *m*/*z* 268 (M^+, 18), 224 (91), 174 (100), 167 (42), 142 (64) and 129 (64).

In a similar manner, compound **20** (25.5 mg, 0.095 mmol) afforded quantitatively a solid which, on recrystallization from hexane, gave (3a*S**,3b*S**,3c*R**,7a*S**,8a*R**)-3c-phenyl-3,3a,3b,3c,4,5,6,7,8,8a-decahydro-1*H*-benzo[1,3]cyclopropa[3,4]cyclopenta[1,2-*c*]furan-3-one **35** (23.6 mg, 92%) as needles, mp 129.5–130 °C (Found: M^+, 268.1441); $\nu_{max}(CHCl_3)/cm^{-1}$ 1748; δ_H 1.22–1.50 (4H, m), 1.72 (1H, ddd, *J* 14.0, 8.5 and 4.5), 1.85 (1H, dd, *J* 8.5 and 8.5), 1.86 (1H, d, *J* 8.5), 1.90–1.98 (2H, m), 2.05 (1H, dd, *J* 15.0 and 10.5), 2.02–2.08 (1H, m), 2.09 (1H, dd, *J* 15.0 and 3.5), 3.20 (1H, ddddd, *J* 12.5, 11.0, 10.5, 8.5 and 3.5), 3.42 (1H, dd, *J* 12.5 and 8.5), 3.72 (1H, dd, *J* 11.0 and 8.5) and 7.13–7.40 (5H, br m); δ_C 21.3 (t), 22.6 (t), 29.1 (t), 36.4 (s), 37.0 (d), 37.8 (t), 39.7 (t), 40.4 (s), 40.7 (d), 47.5 (d), 71.5 (t), 126.8 (d), 128.0 (d), 128.8 (d), 129.9 (d), 130.8 (d), 142.0 (s) and 179.6 (s); *m*/*z* 268 (M^+, 28), 181 (52), 167 (56), 141 (64) and 91 (100).

In a similar manner, compound **18b** (60 mg, 0.28 mmol) afforded quantitatively a solid which, on PTLC (benzene), gave compound **26** and 3′-*phenylspirocyclopentane*-1,4′-*tetrahydrofuran*-2′-*one* **36** (8.0 mg, 13%). The physical and spectral properties of compound **26** were in accord with those of the specimen obtained by the photolysis of compound **11**.

Compound **36**: leaflets, mp 78–79 °C (from cyclohexane) (Found: M^+, 216.1166. $C_{14}H_{16}O_2$ requires *M*, 216.1150); $\nu_{max}(CHCl_3)/cm^{-1}$ 1768; δ_H 1.19–1.28 (1H, m), 1.36–1.66 (5H, m), 1.70–1.84 (2H, m), 3.71 (1H, s), 4.09 (1H, d, *J* 9.0), 4.20 (1H, d, *J* 9.0), 7.13–7.18 (2H, m) and 7.29–7.39 (3H, m); δ_C 23.4 (t), 23.5 (t), 31.3 (t), 35.8 (t), 52.7 (s), 55.1 (d), 76.7 (t), 127.6 (d), 128.6 (d), 129.7 (d), 133.8 (s) and 177.3 (s); *m*/*z* 216 (M^+, 38), 172 (27), 129 (39), 118 (39) 91 (47) and 81 (100).

Catalytic hydrogenation of the hexahydroisobenzofuranone 37

Following the method similar to that used for the preparation of compound **11**, (3a*R**,7*S**,7a*R**)-7-phenyl-1,3,3a,4,7,7a-hexahydroisobenzofuran-1-one **37**[11a] (3.2 g, 15.0 mmol) was hydrogenated, and worked up to give quantitatively a solid which, on recrystallization from diisopropyl ether, gave perhydroisobenzofuranone **22** (2.75 g, 85%) as prisms. The physical and spectral properties of compound **22** were in accord with those of the specimen obtained by the irradiation of compound **11**.

(3a*R,7*S**,7a*S**)-7-Phenyl-1,3,3a,4,7,7a-hexahydroisobenzofuran-1-one 38**

A mixture of the hexahydroisobenzofuranone **37** (400 mg, 1.86 mmol), sodium hydride (60% in liquid paraffin, washed twice with benzene; 85 mg, 2.1 mmol), and THF (10 cm^3) was stirred at room temperature for 30 min. The reaction was quenched by the addition of acetic acid (0.5 cm^3) to the mixture which was then poured into ice-cooled water (30 cm^3) and extracted with diethyl ether. The extract was washed with aq. sodium hydrogen carbonate, and evaporated to give a pale yellow oil (415 mg) which, on recrystallization from hexane–acetone, gave title compound **38** (380 mg, 95%) as colourless needles, mp 136–137 °C (lit.,[11a] mp 137–138 °C) (Found: C, 78.6; H, 6.6%; M^+, 214.1010. $C_{14}H_{14}O_2$ requires C, 78.48; H, 6.59%, *M*, 214.0994); $\nu_{max}(CHCl_3)/cm^{-1}$ 1780; δ_H 2.10–2.60 (4H, m), 3.62 (1H, dm, *J* 11.0), 3.89 (1H, dd, *J* 11.0 and 9.0), 4.43 (1H, dd, *J* 9.0 and 7.0), 5.69 (1H, dm, *J* 10.0), 5.89 (1H, dm, *J* 10.0) and 7.20–7.37 (5H, m); δ_C 27.9 (t), 39.2 (d), 43.1 (d), 47.3 (d), 71.3 (t), 125.9 (d), 126.8 (d), 128.3 (d), 131.8 (d), 141.7 (s) and 175.7 (s); *m*/*z* 214 (M^+, 100), 173 (63), 155 (61), 142 (42), 129 (62), 115 (52) and 91 (59).

Catalytic hydrogenation of the hexahydroisobenzofuranone 38

Following the method similar to that used for the preparation of compound **11**, compound **38** (58.0 mg, 0.27 mmol) was hydrogenated, and worked up to give quantitatively a solid which, on recrystallization from diethyl ether, gave the perhydroisobenzofuranone **23** (52.1 mg, 89%) as prisms. The physical and spectral properties of compound **23** were in accord with those of the specimen obtained by the irradiation of compound **11**.

Birch reduction of compound 11

A solution of compound **11** (50 mg, 0.23 mmol) in THF (5 cm^3) was added to a stirred solution of lithium (20 mg, 2.9 mmol) in liquid ammonia (*ca.* 10 cm^3) at −50 °C. After the deep blue

reaction mixture had turned pale yellow it was treated with ammonium chloride (100 mg, 1.87 mmol) and gently heated to remove the resulting ammonia. After this, the mixture was filtered, and the residue was washed with diethyl ether. The combined filtrate and washings were washed with brine, and evaporated to give a pale yellow oil (43 mg) which, on distillation under reduced pressure, gave the perhydroisobenzofuranone **21** (33 mg, 65%) as an oil, bp 100–102 °C/0.009 mmHg. This material solidified with time.

Compound **21**: needles, mp 79–81 °C (from diisopropyl ether) (Found: C, 77.6; H, 7.5%; M^+, 216.1174. $C_{14}H_{16}O_2$ requires C, 77.75; H, 7.46%; *M*, 216.1150); $\nu_{max}(CHCl_3)/cm^{-1}$ 1768. The spectral properties of compound **21** were in accord with those of the specimen obtained by the irradiation of compound **11**.

Sulfenylation of compound 22

According to a previously described method,[5b] a solution of compound **22** (2.0 g, 9.3 mmol) in THF (20 cm^3) was treated with a solution of lithium isopropylcyclohexylamide [prepared from *N*-isopropylcyclohexylamine (2.36 cm^3, 14.3 mmol) and a 1.6 mol dm^{-3} solution of butyllithium in hexane (8.9 cm^3, 14.2 mmol) in THF (20 cm^3)]. The solution of the lithium enolate thus prepared was added dropwise to a solution of dimethyl disulfide (2.45 cm^3, 27.8 mmol) in THF (10 cm^3) at 0 °C. After being stirred at 0 °C for 5 h, the mixture was poured into brine (30 cm^3) and extracted with benzene. The extract was washed successively with 10% aq. sulfuric acid and brine, and then evaporated to give an orange oil (3.0 g) which on column chromatography (hexane–acetone, 50:1), gave (3aS*,7S*,7aR*)-7a-*methylsulfanyl*-7-*phenyl*-1,3,3a,4,5,6,7,7a-*octahydroisobenzofuran*-1-*one* **39a** (1.82 g, 75%) and its (3aS*,7S*,7aS*)-*isomer* **39b** (72.8 mg, 3%).

Major sulfide **39a**: prisms, mp 76–77 °C (from light petroleum) (Found: C, 68.5; H, 6.9%; M^+, 262.1039. $C_{15}H_{18}O_2S$ requires C, 68.67; H, 6.91%; *M*, 266.1027); $\nu_{max}(CHCl_3)/cm^{-1}$ 1764; δ_H 1.31 (3H, s), 1.43–1.61 (3H, m), 1.81–1.95 (3H, m), 2.04 (1H, dm, *J* 13.0), 2.26 (1H, ddd, *J* 12.0, 6.0 and 4.0), 3.00 (1H, dd, *J* 12.5 and 4.0), 3.80 (1H, d, *J* 8.0), 4.78 (1H, dd, *J* 8.0 and 4.0), 7.22–7.31 (3H, m) and 7.57–7.61 (2H, m); δ_C 14.4 (q), 25.0 (t), 29.5 (t), 30.1 (t), 45.1 (d), 53.1 (d), 54.5 (s), 71.0 (t), 126.9 (d), 127.3 (d), 130.8 (d), 140.1 (s) and 171.5 (s); *m*/*z* 262 (M^+, 100), 216 (69), 169 (22), 144 (26), 130 (56), 115 (48) and 91 (88).

Minor sulfide **39b**: prisms, mp 154–155 °C (from light petroleum) (Found: C, 68.45; H, 6.9%; M^+, 262.1033); $\nu_{max}(CHCl_3)/cm^{-1}$ 1768; δ_H 1.41 (1H, ddddd, *J* 13.5, 13.5, 13.0, 4.5 and 4.5), 1.43 (3H, s), 1.58 (1H, dddd, *J* 13.0, 13.0, 13.0 and 4.0), 1.68 (1H, dm, *J* 13.0), 1.77 (1H, dm, *J* 13.5), 1.96 (1H, dm, *J* 13.5), 2.44–2.55 (2H, m), 3.07 (1H, dd, *J* 12.5 and 3.5), 4.20 (1H, dd, *J* 8.0 and 6.5), 4.42 (1H, dd, *J* 11.0 and 8.0), 7.23–7.32 (3H, m) and 7.49–7.53 (2H, m); δ_C 14.2 (q), 22.0 (t), 25.7 (t), 28.1 (t), 48.6 (d), 49.8 (d), 55.2 (s), 69.1 (t), 127.1 (d), 127.4 (d), 130.0 (d), 139.1 (s) and 172.0 (s); *m*/*z* 262 (M^+, 100), 216 (16), 169 (15), 144 (27), 129 (30), 115 (30) and 91 (61).

Sodium metaperiodate oxidation of the sulfide 39a

A mixture of the sulfide **39a** (590 mg, 2.25 mmol), sodium metaperiodate (730 mg, 3.14 mmol), THF (15 cm^3) and water (15 cm^3) was heated at 80 °C for 5 h. After being cooled, the mixture was poured into ice–water (50 cm^3) and extracted with diethyl ether. The extract was washed successively with aq. sodium thiosulfate–sodium hydrogen carbonate and brine, and evaporated to give an orange oil (585 mg) which, on column chromatography (hexane–acetone, 20:1), gave compound **11** (285 mg, 59%) and its regioisomer **25** (111 mg, 23%). The spectral properties of the major product **11** were in accord with those of the specimen synthesized by catalytic hydrogenation of compound **10b**, and the minor one with the photoproduct **25** obtained by the irradiation of compound **11**.

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