

# Furan-2(3*H*)- and -2(5*H*)-ones. Part 8.<sup>1</sup> Conformation and di- $\pi$ -methane reactivity of the 4,7-disubstituted tetrahydroisobenzofuran-1-one system: a mechanistic and exploratory study

Osamu Muraoka,<sup>\*,a</sup> Genzoh Tanabe,<sup>a</sup> Emi Yamamoto,<sup>a</sup> Masaru Ono,<sup>a</sup> Toshie Minematsu<sup>a</sup> and Takayoshi Kimura<sup>b</sup>

<sup>a</sup> Faculty of Pharmaceutical Sciences, Kinki University and Faculty of Sciences and Technologies, Kinki University,<sup>b</sup> Kowakae 3-4-1, Higashi-osaka, Osaka 577, Japan

Photoirradiation of *cis*- and *trans*-4,7-diphenyl-1,3,4,7-tetrahydroisobenzofuran-1-one *cis*- and *trans*-**14** and its 4-methyl analogues *cis*- and *trans*-**15** afford the corresponding di- $\pi$ -methane rearrangement products **27**, **28** and **24** in moderate yields. MM2 calculations for the *cis*- and *trans*-4,7-diphenyl substrates *cis*- and *trans*-**14** showed that the planar structure is most stable for both compounds and that the molecular energy difference between the planar structure and the boat conformation is small enough for a boat–planar–boat conversion. On the basis of the calculations, the di- $\pi$ -methane rearrangement of the compounds **14** and **15** is supposed to proceed *via* the boat conformation with a pseudoaxial phenyl substituent. An X-ray structure determination of the two diphenyl substrates *cis*- and *trans*-**14** provides strong support for the validity of the calculations in predicting optimum structures for *cis*- and *trans*-disubstituted tetrahydroisobenzofuranone.

## Introduction

The establishment of the general structural factors which influence excited state reactivity is one of the prime goals of organic photochemistry. In a previous paper, we reported the regio-specific di- $\pi$ -methane rearrangement of  $\beta$ -apolignans **1** into the corresponding tetrahydrocycloprop[*a*]indenes **2** and showed that the rearrangement is common among  $\beta$ -apolignans irrespective of their ring substituents; we also showed that only the phenyl substituent migrates among the three possible di- $\pi$ -methane systems found in the  $\beta$ -apolignans **1**.<sup>2</sup> 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 the cyclopropane lactone **4** as the sole rearrangement product.<sup>3</sup> 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- $\pi$ -methane rearrangement to afford a cyclopropano lactone **7** (R = Ph) in moderate yield.<sup>4</sup> On the other hand, upon irradiation of 4-benzyl counterparts **8**, characteristic acceleration of the di- $\pi$ -methane rearrangement was observed upon introduction of any alkyl substituent at the 'central methane' carbon to afford the corresponding cyclopropano lactones **9** in good yields.<sup>5</sup> These observations suggested that the stereochemical rigidity of  $\beta$ -apolignans **1** could be responsible for the efficient regioselectivity of the rearrangement. Thus, two substrates **10** and **11** having such rigidity were next examined, and we showed that the former, **10**, afforded the corresponding di- $\pi$ -methane rearrangement product **12**, while its dihydro analogue **11** produced mainly photo-reduced products **13**.<sup>1</sup> Since compound **10** was suggested to be in rapid boat-to-boat interconversion in solution (see Scheme 1), it was postulated that the rearrangement had been caused by the interaction of the two  $\pi$ -orbitals through the boat **A** conformation where the pendant phenyl is pseudoaxially oriented.<sup>1</sup> In order to gain further insight into the relationship

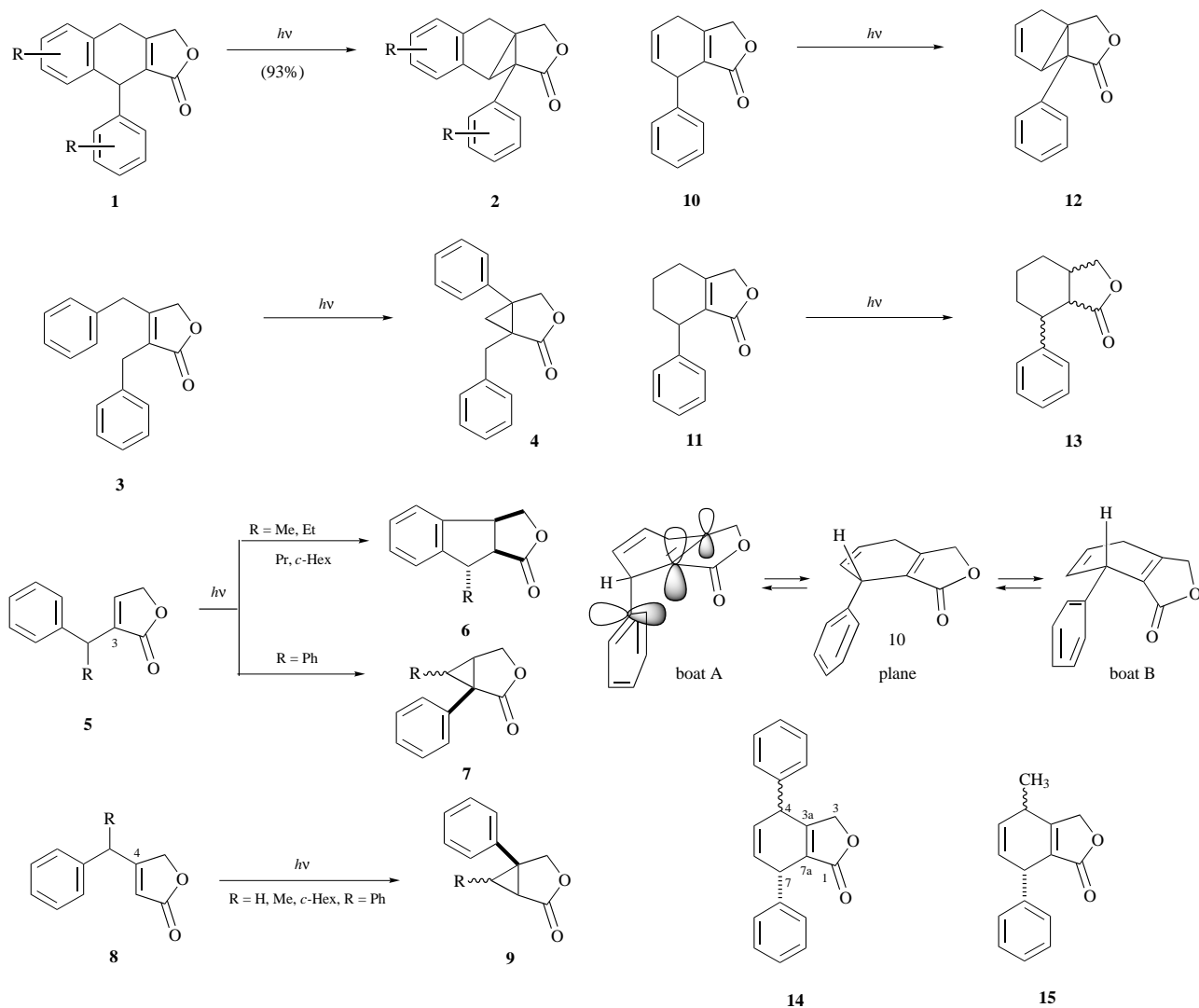
between the photoreactivity and the stereochemical features of the tetrahydroisobenzofuranone system, we examined the photo-reaction of the system bearing a substituent at the C-4 position, *cis*- and *trans*-4,7-diphenyl-1,3,4,7-tetrahydroisobenzofuran-1-one *cis*- and *trans*-**14**, and their 4-methyl analogues, *cis*- and *trans*-4-methyl-7-phenyl-1,3,4,7-tetrahydroisobenzofuran-1-one *cis*- and *trans*-**15**. We presumed that for the *cis*-substrates *cis*-**14** and *cis*-**15** the boat **A** conformation is little involved because of the transannular steric effect between the two substituents at the C-4 and C-7 positions, while for the *trans*-isomers *trans*-**14** and *trans*-**15** it would be. Compound **3** had afforded compound **4**, a phenyl migration product at the  $\beta$ -ketonic position upon irradiation;<sup>3</sup> therefore, the migration aptitude of the two phenyl moieties in compounds **14** is also of interest.

## Results

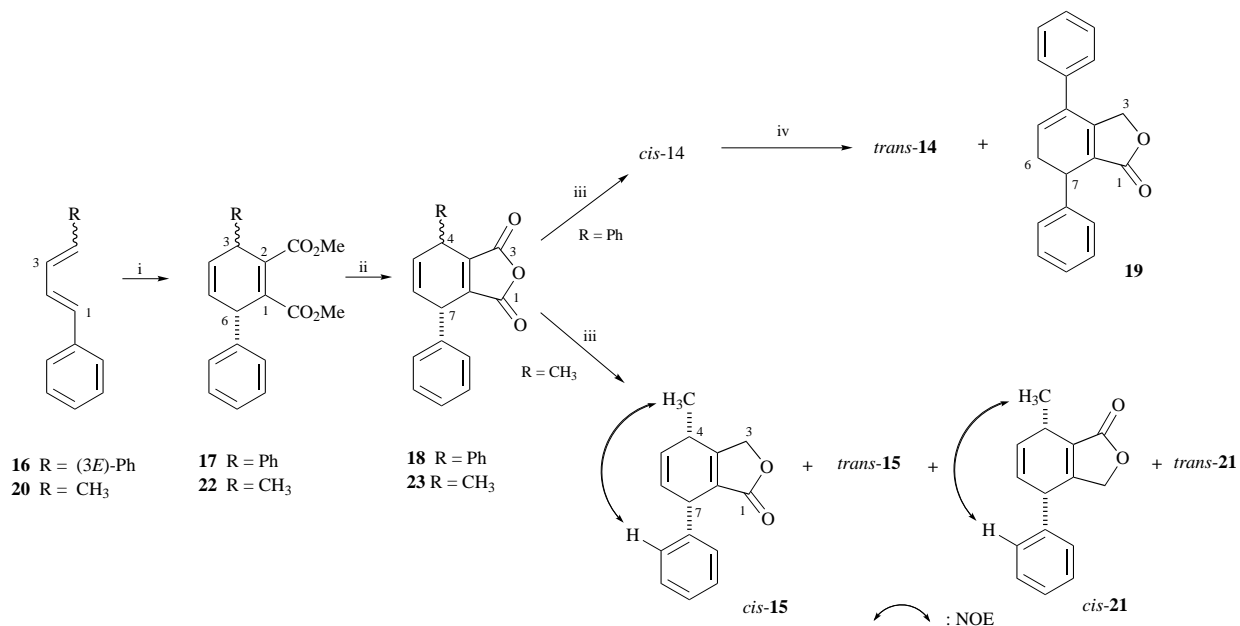
### Synthesis of the photochemical substrates **14** and **15**

The Diels–Alder reaction of (1*E*, 3*E*)-1,4-diphenylbuta-1,3-diene **16**<sup>6</sup> with dimethyl acetylenedicarboxylate (DMAD) gave a 1,4-adduct, dimethyl *cis*-3,6-diphenylcyclohexa-1,4-diene-1,2-dicarboxylate *cis*-**17**<sup>6</sup> (90%). Treatment of this with perchloric acid in formic acid<sup>7</sup> followed by sodium boranuide reduction of the resulting anhydride, *cis*-4,7-diphenyl-1,3,4,7-tetrahydroisobenzofuran-1,3-dione *cis*-**18**, gave the desired lactone *cis*-**14** (78%). It is interesting to note that the lactone *cis*-**14**, when treated with 1,4-diazabicyclo[2.2.2]octane (DABCO) in methanol, afforded the corresponding *trans*-isomer *trans*-**14** (17%), although isomerisation of the double bond predominated to produce a conjugated diene, 4,7-diphenyl-1,3,6,7-tetrahydroisobenzofuran-1-one **19**, as the main product (66%) with recovery of a small amount of the starting material *cis*-**14** (12%). Prolonged reaction resulted in the increased formation of the undesirable dienone **19** (80%).

4-Methyl-substituted analogues *cis*- and *trans*-**15** were prepared in a similar manner starting from a *ca.* 5:1 mixture of (1*E*,3*E*)- and (1*E*,3*Z*)-1-phenylpenta-1,3-diene (3*E*)- and (3*Z*)-**20**,<sup>8</sup> as a mixture with their regioisomers, *cis*- and *trans*-7-methyl-4-phenyl-1,3,4,7-tetrahydroisobenzofuran-1-one *cis*- and *trans*-**21**, in 45, 9, 18, and 3% overall yields, respectively, *via*



Scheme 1



Scheme 2 Reagents and conditions: i, DMAD, 150 °C or benzene, reflux; ii, HClO<sub>4</sub>, HCO<sub>2</sub>H, reflux; iii, NaBH<sub>4</sub>; iv, DABCO, MeOH, room temp.

the corresponding 1,4-adducts, dimethyl 3-methyl-6-phenylcyclohexa-1,4-diene-1,2-dicarboxylate **22**, and anhydrides, 4-methyl-7-phenyl-1,3,4,7-tetrahydroisobenzofuran-1,3-dione **23**. When a *ca.* 1:5.5 mixture of *cis*- and *trans*-dienes *cis*- and

*trans*-**20** was employed as the starting material, the *trans*-isomer *trans*-**15** was obtained as the major product (50%).

Both *cis*- and *trans*-diphenyl compounds *cis*- and *trans*-**14** displayed three characteristic IR absorptions at 1633, 1688 and

**Table 1**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra for the 1,3,4,7-tetrahydroisobenzofuranones **14** and **15**

Position	<i>cis</i> - <b>14</b>		<i>trans</i> - <b>14</b>	
	$\delta_{\text{H}}^a$	$\delta_{\text{C}}^b$	$\delta_{\text{H}}$	$\delta_{\text{C}}$
1		172.2 (s)		172.2 (s)
3	4.52 dd 17.0, 1.0 4.72 dd 17.0, 1.5	70.6 (t)	4.38 dd 17.5, 2.0 4.71 dd 17.5, 1.0	70.4 (t)
3a		159.6 (s)		159.7 (s)
4	4.39 br d-like 7.0	42.5 (d)	4.39–4.45 m	42.4 (d)
5	5.90 dd 10.0, 1.5	125.5 (d)	5.93 ddd 10.0, 3.0, 1.5	125.8 (d)
6	5.99 dd 10.0, 1.5	128.8 (d)	6.03 ddd 10.0, 3.0, 2.0	128.74 (d)
7	4.37 br d-like 7.0	39.1 (d)	4.39–4.45 m	39.1 (d)
7a		126.3 (s)		126.5 (s)
Arom.	7.23–7.42 (10H, m)	127.1 (d), 127.76 (d) 127.84 (d), 128.3 (d) 128.6 (d), 129.3 (d) 139.8 (s), 140.2 (s)	7.16–7.41 (10H, m)	127.2 (d), 127.88 (d) 127.93 (d), 128.3 (d) 128.66 (d), 129.3 (d) 140.2 (s)

Position	<i>cis</i> - <b>15</b>		<i>trans</i> - <b>15</b>	
	$\delta_{\text{H}}$	$\delta_{\text{C}}$	$\delta_{\text{H}}$	$\delta_{\text{C}}$
Me	1.36 d 7.0	20.5 (q)	1.29 d 7.0	19.8 (q)
1		172.5 (s)		172.4 (s)
3	4.71 ddd 17.0, 2.5, 1.0 4.86 dd 17.0, 1.5	70.4 (t)	4.76 ddd 17.0, 1.5 $\times$ 2 4.85 dd 17.0, 2.5	70.1 (t)
3a		161.9 (s)		161.8 (s)
4	3.23 br qdm 7.0 $\times$ 2	30.6 (d)	3.33 br qdm 7.0 $\times$ 2	30.4 (d)
5	5.80 dm 10.0	127.8 (d)	5.78 ddd 10.0, 2.5, 1.5	127.9 (d)
6	5.83 dm 10.0	128.0 (d)	5.85 ddd 10.0, 3.5, 2.0	128.1 (d)
7	4.26 br dm 7.0	39.3 (d)	4.24 br m	39.1 (d)
7a		126.0 (s)		126.0 (s)
Arom.	7.20–7.26 (3H, m) 7.28–7.32 (2H, m)	126.9 (d) 128.3 (d) 128.5 (d) 140.2 (s)	7.19–7.24 (3H, m) 7.27–7.31 (2H, m)	127.0 (d) 128.2 (d) 128.5 (d) 140.6 (s)

<sup>a</sup> $^1\text{H}$  chemical shift values ( $\delta$  ppm from SiMe<sub>4</sub>) are followed by multiplicity of the signals and coupling constants ( $J/\text{Hz}$ ). <sup>b</sup> Letters s, d, t and q in parentheses indicate quaternary, tertiary, secondary and methyl carbons, respectively.

1750–1760 cm<sup>-1</sup> corresponding to the dienone system. In the  $^1\text{H}$  NMR spectrum of the *cis*-isomer *cis*-**14**, characteristic homoallylic coupling ( $J_{4,7}$  7.0 Hz) was observed, while the corresponding coupling was not detected with respect to the *trans*-isomer *trans*-**14** because of overlapping of signals due to protons at C-4 and C-7. Although both  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopic properties were consistent with the 4,7-diphenylisobenzofuranone structure **14** (Table 1), it was difficult to discriminate unambiguously between these two isomers *cis*- and *trans*-**14**. Thus, final structural confirmation was established by the X-ray crystallographic analysis (see Discussion).

The  $^1\text{H}$  NMR spectrum of compound **19** displayed only a single olefinic signal at  $\delta_{\text{H}}$  6.28, and signals due to methylene protons at C-6 appeared as an AB-type quartet at  $\delta_{\text{H}}$  2.95 and 3.12. Four singlets at  $\delta_{\text{C}}$  126.0, 133.5, 156.0 and 172.9 and a doublet at  $\delta_{\text{C}}$  132.6 corresponded to the conjugated dienone carbons, whose correlation was confirmed on the basis of an incredible natural abundance double quantum transfer experiment (INADEQUATE).

Spectroscopic properties of their methyl analogues *cis*- and *trans*-**15** were correlated with those of the diphenyl counterparts *cis*- and *trans*-**14** as shown in Table 1. With respect to the *cis*-isomer *cis*-**15**, a considerable nuclear Overhauser effect (NOE) has been detected between the methyl and aromatic protons at the *ortho*-position as shown in Scheme 2, supporting the depicted configuration. In the  $^1\text{H}$  NMR spectra of their regioisomers *cis*- and *trans*-**21**, signals due to the lactonic methylene moiety shifted upfield due to anisotropy of the phenyl group.

#### Photolysis of the *cis*- and *trans*-lactones **14** and **15**

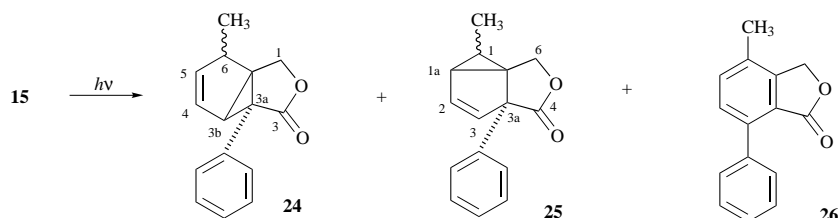
Upon irradiation in methanol, both *cis*- and *trans*-4-methyl substrates *cis*- and *trans*-**15** showed similar photoreactivity with each other, giving 6 $\alpha$ - and 6 $\beta$ -methyl-3 $\alpha\alpha$ -phenyl-3,3a,3b,

6-tetrahydro-1*H*-cyclopenta[1,3]cyclopropa[1,2-*c*]furan-3-one 6 $\alpha$ - and 6 $\beta$ -**24**, in 22% yield each, the efficiency of the rearrangement having decreased compared to that of the rearrangement of compound **10**. Additionally, formation of isomeric photorearrangement products, 1 $\alpha$ - and 1 $\beta$ -methyl-3 $\alpha\alpha$ -phenyl-1,1a,3a,4-tetrahydro-6*H*-cyclopropa[1,5]cyclopenta[1,2-*c*]furan-4-one 1 $\alpha$ - and 1 $\beta$ -**25** and a dehydrogenated product, 4-methyl-7-phenyl-1,3-dihydroisobenzofuran-1-one **26**, were produced with recovery of 32% of the reactant *trans*-**15**. Prolonged reaction caused decomposition of the photo-products.

Upon irradiation of the *trans*-diphenyl lactone *trans*-**14** in methanol, two expected rearrangement products, 3 $\alpha\alpha$ ,6 $\beta$ -diphenyl-3,3a,3b,6-tetrahydro-1*H*-cyclopenta[1,3]cyclopropa[1,2-*c*]furan-3-one 6 $\beta$ -**27** and 3 $\alpha\alpha$ ,6 $\beta$ -diphenyl-3,3a,3b,6-tetrahydro-1*H*-cyclopenta[1,3]cyclopropa[1,2-*c*]furan-1-one 6 $\beta$ -**28**, were obtained in 36 and 14% yields, respectively, after 9 h of irradiation. Additionally, formation of a small amount of the isomeric photorearrangement products, 1 $\alpha$ ,3 $\alpha\alpha$ - and 1 $\beta$ ,3 $\alpha\alpha$ -diphenyl-1,1a,3a,4-tetrahydro-6*H*-cyclopropa[1,5]cyclopenta[1,2-*c*]furan-4-one 1 $\alpha$ - and 1 $\beta$ -**29**, and a dehydrogenated product, 4,7-diphenyl-1,3-dihydroisobenzofuran-1-one **30** was also detected.

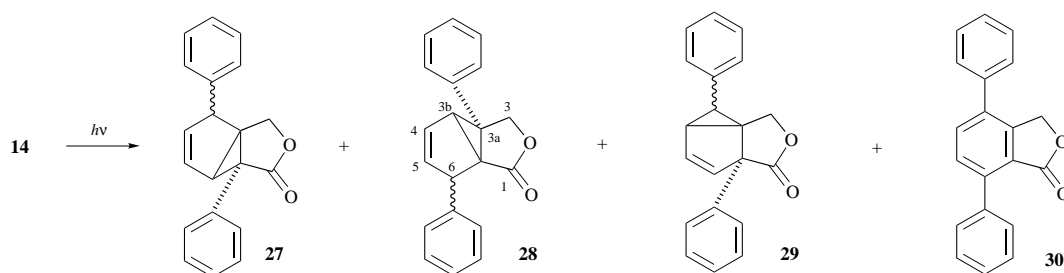
Upon irradiation of the *cis*-isomer *cis*-**14** under the same conditions, a mode of rearrangement similar to that of the *trans*-counterpart *trans*-**14** was observed, giving 6 $\alpha$ -isomers of cyclopropano lactones, 3 $\alpha\alpha$ ,6 $\alpha$ -diphenyl-3,3a,3b,6-tetrahydro-1*H*-cyclopenta[1,3]cyclopropa[1,2-*c*]furan-3-one 6 $\alpha$ -**27** and 3 $\alpha\alpha$ ,6 $\alpha$ -diphenyl-3,3a,3b,6-tetrahydro-1*H*-cyclopenta[1,3]cyclopropa[1,2-*c*]furan-1-one 6 $\alpha$ -**28** in 28 and 5% yields, respectively.

Upon acetone-sensitised irradiation, reactions proceeded more effectively with all reactants **14** and **15**, affording the same



**Table 2**

Substrate	Solvent	Reaction time ( <i>t</i> /h)	Products (isolated yield %)					
			6 $\alpha$ - <b>24</b>	6 $\beta$ - <b>24</b>	1 $\alpha$ - <b>25</b>	1 $\beta$ - <b>25</b>	<b>26</b>	Recovered
<i>trans</i> - <b>15</b>	Methanol	15	—	22	2	6	9	32
<i>trans</i> - <b>15</b>	Acetone	3	—	18	4	3	9	27
<i>cis</i> - <b>15</b>	Methanol	15	22	—	6	1	7	32
<i>cis</i> - <b>15</b>	Acetone	3	25	—	7	3	9	21



**Table 3**

Substrate	Solvent	Reaction time ( <i>t</i> /h)	Products (isolated yield %)							Recovered
			6 $\alpha$ - <b>27</b>	6 $\beta$ - <b>27</b>	6 $\alpha$ - <b>28</b>	6 $\beta$ - <b>28</b>	1 $\alpha$ - <b>29</b>	1 $\beta$ - <b>29</b>	<b>30</b>	
<i>trans</i> - <b>14</b>	Methanol	9	—	36	—	14	1	2	3	21
<i>trans</i> - <b>14</b>	Acetone	3	—	20	—	14	1	3	7	21
<i>cis</i> - <b>14</b>	Methanol	9	28	—	5	—	8	2	8	28
<i>cis</i> - <b>14</b>	Acetone	3	21	—	3	—	10	2	6	23

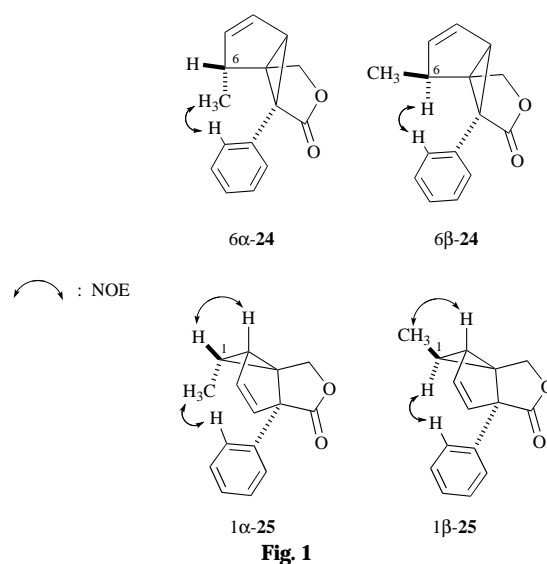
**Scheme 3**

members of photoproducts in a shorter reaction time. Results of the irradiations are summarised in Table 2 and 3 in Scheme 3.

The minor photoproducts 1 $\alpha$ - and 1 $\beta$ -**29** interconverted with each other when irradiated under the acetone-sensitised conditions, and transformation of compounds 1 $\alpha$ - and 1 $\beta$ -**29** to their isomeric cyclopropano lactones **27** was also detected on irradiation. Meanwhile, compounds **27** were unaffected by irradiation, and no reverse transformation leading to compounds **29** was detected. Methyl analogues *cis*- and *trans*-**25** also showed similar photochemical behaviour to compounds *cis*- and *trans*-**29**, and so did compounds **24** to compounds **27**.

#### Structural elucidation of photoproducts

The rearrangement products **24** and **25** showed similar spectroscopic properties. Their molecular weights, which are equal to the reactant **15**, implied the formation of an additional ring system; introduction of a cyclopropano ring has been suggested on the basis of <sup>1</sup>H NMR signals in the highfield region. Formation of the fused cyclopenteno ring was evident on the basis of the small *cis*-vinylic coupling constants, *i.e.*, *ca.* 5.5 Hz each for *J*<sub>4,5</sub> of compounds **24** and *J*<sub>2,3</sub> of compound **25** compared with 10.0 Hz for *J*<sub>5,6</sub> of the cyclohexeno moiety in the reactant **15**. Compound **24** was unambiguously distinguished from compound **25** on the basis of their <sup>1</sup>H NMR spectroscopic properties; the former showed a single signal due to the sole cyclopropano ring proton, while the latter showed two kinds of signals due to protons at C-1 and C-1a (Table 4). The configuration of the methyl group in compounds **24** and **25** was determined on the basis of NOE experiments (see Fig. 1).



**Fig. 1**

Although the stereochemistry of two diphenyl photoproducts of 6 $\beta$ -**27** and 6 $\beta$ -**28** were deducible from NOE experiment as shown in Scheme 4, it was found difficult to discriminate unambiguously between these two photoproducts from the spectroscopic properties. Therefore, rigorous structural assignments for these two isomers 6 $\beta$ -**27** and 6 $\beta$ -**28** were achieved on the basis of degradation studies (see Scheme 4). Thus, hydrogenolysis of compound 6 $\beta$ -**27** was carried out over palladium-on-carbon to give 3 $\alpha$ ,6 $\beta$ -diphenyl-3,3a,3b,4,5,6-hexahydro-

**Table 4**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra for the photoproducts **24** and **25**

Position	6 $\alpha$ - <b>24</b>		6 $\beta$ - <b>24</b>	
	$\delta_{\text{H}}^a$	$\delta_{\text{C}}^b$	$\delta_{\text{H}}$	$\delta_{\text{C}}$
1	4.43 d 9.5 4.60 d 9.5	68.4 (t)	4.51 d 9.0 4.70 d 9.0	68.0 (t)
3		176.7 (s)		175.8 (s)
3a		44.9 (s)		44.6 (s)
3b	2.55 br s-like	38.1 (d)	2.61 dd 2.5, 2.0	38.7 (d)
4	5.90 dm 5.5	127.4 (d)	5.74 dm 5.5	127.1 (d)
5	5.47 dd 5.5, 2.0	138.7 (d)	5.42 dd 5.5, 2.0	138.6 (d)
6	3.24 qm 7.5	40.8 (d)	2.70 qm 7.5	39.7 (d)
6a		41.7 (s)		41.6 (s)
Me	1.00 d 7.5	12.4 (q)	1.14 d 7.5	15.8 (q)
Arom.	7.17–7.23 (2H, m) 7.24–7.34 (3H, m)	127.7 (d), 128.1 (d) 131.5 (s), 133.1 (d)	7.13–7.19 (2H, m) 7.25–7.32 (3H, m)	127.8 (d), 128.3 (d) 130.6 (s), 131.6 (d)
Position	1 $\alpha$ - <b>25</b>		1 $\beta$ - <b>25</b>	
	$\delta_{\text{H}}$	$\delta_{\text{C}}$	$\delta_{\text{H}}$	$\delta_{\text{C}}$
1	1.66 br qd 9.0, 6.5	21.0 (d)	1.05 qd 6.0, 3.5	25.5 (d)
1a	2.18 dd 9.0, 2.0	36.2 (d)	1.81 dd 3.5, 2.0	38.4 (d)
2	5.88 ddd 5.5, 2.0, 1.0	131.2 (d)	6.14 ddd 5.5, 2.0, 1.0	136.2 (d)
3	6.19 dd 5.5, 1.0	133.4 (d)	5.82 d 5.5	131.2 (d)
3a		62.6 (s)		64.4 (s)
4		177.0 (s)		177.6 (s)
6	4.20 d 9.0 4.85 d 9.0	72.8 (t)	4.42 d 9.0 4.80 d 9.0	70.2 (t)
6a		34.1 (s)		35.9 (s)
Me	0.72 d 6.5	8.3 (q)	1.17 d 6.0	13.1 (q)
Arom.	7.25–7.40 (3H, m) 7.42–7.48 (2H, m)	127.0 (d), 127.7 (d) 128.7 (d), 135.3 (s)	7.25–7.42 (5H, m)	126.6 (d), 127.7 (d) 129.0 (d), 137.2 (s)

<sup>a</sup>  $^1\text{H}$  chemical shift values ( $\delta$  ppm from  $\text{SiMe}_4$ ) are followed by multiplicity of the signals and coupling constants ( $J/\text{Hz}$ ). <sup>b</sup> Letters s, d, t and q in parentheses indicate quaternary, tertiary, secondary and methyl carbons, respectively.

1*H*-cyclopenta[1,3]cyclopropa[1,2-*c*]furan-3-one **31** (89%) with the concomitant formation of a spiro compound, 2,3'-diphenylspirocyclopentane-1,4'-tetrahydrofuran-2'-one **32** (5%). In the  $^1\text{H}$  NMR spectrum of the minor product **32**, a one-proton singlet at  $\delta_{\text{H}}$  3.52, a signal typical for the  $\alpha$ -methine proton of the phenyl acetate system, was detected, supporting the depicted structure **32**, a product of cyclopropano ring-cleavage at the C(3a)–C(3b) bond in compound 6 $\beta$ -**27**.

The regioisomer 6 $\beta$ -**28** gave the corresponding reduced product, 3a $\beta$ ,6 $\alpha$ -diphenyl-3,3a,3b,4,5,6-hexahydro-1*H*-cyclopenta[1,3]cyclopropa[1,2-*c*]furan-3-one **33** in 92% yield. No evidence for the formation of a product of cyclopropano ring-cleavage was detected in spite of careful examination of the reaction.

In the  $^1\text{H}$  NMR spectra of compounds 6 $\beta$ -**27** and 6 $\beta$ -**28**, a significant upfield shift owing to the shielding effect of the phenyl moiety at C-3a was observed with respect to the signals due to C-6 protons (at  $\delta_{\text{H}}$  3.70 and 3.63, respectively), while those due to the corresponding protons of their 6 $\alpha$ -isomers 6 $\alpha$ -**27** and 6 $\alpha$ -**28** were observed at  $\delta_{\text{H}}$  4.46 and 5.00, respectively, indicating the depicted configuration of the 6 $\beta$ -isomers in Scheme 4.

The 6 $\alpha$ -isomers 6 $\alpha$ -**27** and 6 $\alpha$ -**28** were distinguished from each other on the basis of chemical shifts of the signals due to C-6 methine protons; the signal which appeared at  $\delta_{\text{H}}$  4.46 was assigned to one of the protons in compound 6 $\alpha$ -**27**, and one at  $\delta_{\text{H}}$  5.00 to compound 6 $\alpha$ -**28**, the downfield shift of which would be rationalised in terms of the anisotropy of the lactone carbonyl moiety. Signals due to aromatic protons at the *ortho* position in both phenyl rings shifted upfield to  $\delta_{\text{H}}$  6.53–6.76 as a result of the anisotropy of the facing phenyl moiety; this also supported the assigned *cis*-stereochemistry.

The configuration of the phenyl group in the cyclopropano lactones 1 $\alpha$ - and 1 $\beta$ -**29** was determined on the basis of vicinal coupling constants between the C-1 and C-1a protons. The

signal with a larger coupling constant ( $J_{1,1a}$  8.5 Hz)† was assigned to compound 1 $\alpha$ -**29**, while that with the smaller constant ( $J_{1,1a}$  3.5 Hz)† was assigned to the *trans*-isomer 6 $\beta$ -**29**. Further support for the assignments made was given by differential NOE experiments (see Scheme 4).

Exposure of the two stereoisomers 1 $\alpha$ - and 1 $\beta$ -**29** to hydrogenolysis afforded the same degradation product, 3a-benzyl-6a-phenylhexahydro-1*H*-cyclopenta[*c*]furan-1-one **34** in 90 and 89% yields from compounds 1 $\alpha$ - and 1 $\beta$ -**29**, respectively. Compound **34** displayed an AB quartet at  $\delta_{\text{H}}$  2.11 and 2.27 arising from benzylic methylene protons, and the relative stereochemistry of the methylene moiety and the phenyl group at C-6a was found to be in a *cis* relationship on the basis of NOE enhancements as shown in Scheme 4.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectral data for compounds **27**, **28** and **29** are listed in Table 5.

## Discussion

In our preceding studies, compound **10** was found to afford the phenyl migration product **12** in 43–48% yield.<sup>1</sup> Both 4-phenyl- and 4-methyl-substrates **14** and **15** have shown similar photo-reactivity to that of compound **10**, giving the di- $\pi$ -methane rearrangement products as the major product. Unexpectedly, compounds *cis*-**14** and *cis*-**15** have also afforded the corresponding di- $\pi$ -methane rearrangement products 6 $\alpha$ -**27** and 6 $\alpha$ -**24**, respectively. With respect to 4-methyl-substrates **15** no difference in photoreactivity was observed between the *cis*- and the *trans*-isomer *cis*- and *trans*-**15**, although the efficiency of the rearrangement decreased as compared with compound **10**.

Upon irradiation of the 4,7-diphenyl substrates *cis*- and

† Generally, coupling constants of corresponding protons in cyclopropyl systems have been reported as follows:  $J_{cis}$  = 6–10 Hz and  $J_{trans}$  = 3–5 Hz. (ref. 10).

**Table 5**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra for the photoproducts **27**, **28** and **29**

Position	<b>6<math>\alpha</math>-27</b>		<b>6<math>\beta</math>-27</b>	
	$\delta_{\text{H}}^a$	$\delta_{\text{C}}^b$	$\delta_{\text{H}}$	$\delta_{\text{C}}$
1	4.63 d 9.0 4.79 d 9.0	68.8 (t)	4.01 d 10.0 4.31 d 10.0	68.5 (t)
3		176.1 (s)		175.5 (s)
3a		43.4 (s)		46.1 (s)
3b	2.61 br s-like	38.0 (d)	2.70 dd 2.5, 2.0	38.9 (d)
4	6.16 dm 5.5	129.92 (d)	6.03 dm 5.5	129.1 (d)
5	5.87 dd 5.5, 2.0	136.4 (d)	5.50 dd 5.5, 2.0	136.3 (d)
6	4.46 br ddd 2.5, 2.0 $\times$ 2	50.7 (d)	3.70 ddd 2.5, 2.0 $\times$ 2	51.0 (d)
6a		41.9 (s)		42.9 (s)
Arom.	6.53–6.57 (2H, m) 6.63–6.67 (2H, m) 7.04–7.21 (6H, m)	127.0 (d), 127.4 (d) 127.7 (d), 128.1 (d) 128.2 (d), 129.86 (s) 133.0 (d), 136.8 (s)	7.20–7.26 (2H, m) 7.24–7.28 (2H, m) 7.28–7.40 (6H, m)	127.8 (d), 128.1 (d) 128.3 (d), 128.5 (d) 128.9 (d), 130.5 (s) 131.7 (d), 137.5 (s)

Position	<b>6<math>\alpha</math>-28</b>		<b>6<math>\beta</math>-28</b>	
	$\delta_{\text{H}}$	$\delta_{\text{C}}$	$\delta_{\text{H}}$	$\delta_{\text{C}}$
1		175.6 (s)		172.4 (s)
3	4.30 d 10.0 4.35 dd 10.0, 1.5	76.0 (t)	4.29 d 10.0 4.39 d 10.0	73.4 (t)
3a		42.1 (s)		42.3 (s)
3b	2.73 dd 2.0 $\times$ 2	43.2 (d)	2.90 dd 3.0, 2.0	43.4 (d)
4	6.01 ddd 5.5, 2.0 $\times$ 2	128.3 (d)	5.99 ddd 5.5, 2.0 $\times$ 2	127.7 (d)
5	5.83 dd 5.5, 2.0	135.5 (d)	5.33 dd 5.5, 2.0	136.2 (d)
6	5.00 br s-like	49.2 (d)	3.63 ddd 3.0, 2.0 $\times$ 2	50.2 (d)
6a		44.4 (s)		46.0 (s)
Arom.	6.64–6.68 (2H, m) 6.73–6.76 (2H, m) 7.00–7.16 (6H, m)	126.6 (d), 127.4 (d) 127.86 (d), 128.90 (d) 131.9 (d), 132.0 (s) 137.7 (s)	7.22–7.24 (2H, m) 7.28–7.32 (2H, m) 7.26–7.41 (6H, m)	127.4 (d), 128.06 (d) 128.13 (d), 128.8 (d) 129.0 (d), 130.9 (d) 133.5 (s), 137.1 (s)

Position	<b>1<math>\alpha</math>-29</b>		<b>1<math>\beta</math>-29</b>	
	$\delta_{\text{H}}$	$\delta_{\text{C}}$	$\delta_{\text{H}}$	$\delta_{\text{C}}$
1	2.72 br d 8.5	32.1 (d)	2.16 br d 3.5	29.7 (d)
1a	2.49 dd 8.5, 2.0	37.0 (d)	2.64 dd 3.5, 2.0	35.6 (d)
2	6.26 ddd 5.5, 2.0, 1.0	133.6 (d)	6.28 ddd 5.5, 2.0, 1.0	135.9 (d)
3	5.98 dd 5.5, 1.0	133.2 (d)	6.00 d 5.5	132.2 (d)
3a		63.2 (s)		65.4 (s)
4		177.3 (s)		177.6 (s)
6	4.38 d 9.5 5.09 d 9.5	72.6 (t)	4.41 d 9.5 4.61 d 9.5	69.9 (t)
6a		37.9 (s)		37.1 (s)
Arom.	6.57–6.60 (2H, m) 6.61–6.64 (2H, m) 6.86–7.14 (6H, m)	126.0 (d), 126.5 (d) 127.2 (d), 127.4 (d) 128.3 (d), 130.9 (d) 131.9 (s), 136.0 (s)	7.06–7.10 (2H, m) 7.23–7.36 (6H, m) 7.39–7.44 (2H, m)	126.7 (d), 126.96 (d) 127.02 (d), 127.9 (d) 128.8 (d), 129.1 (d) 136.3 (s), 137.0 (s)

<sup>a</sup>  $^1\text{H}$  chemical shift values ( $\delta$  ppm from  $\text{SiMe}_4$ ) are followed by multiplicity of the signals and coupling constants ( $J/\text{Hz}$ ). <sup>b</sup> Letters s, d, t and q in parentheses indicated quaternary, tertiary, secondary and methyl carbons, respectively.

*trans*-**14**, the rearrangement was observed in both di- $\pi$ -methane systems [C(3a)=C(7a)–C(7)–phenyl and C(7a)=C(3a)–C(4)–phenyl] to give two isomeric rearrangement products **27** and **28**, formation of the former having been favoured. In order to explain these variations observed in photochemical reactivity, the stereochemical properties of the photo-substrates **14** and **15** have been examined.

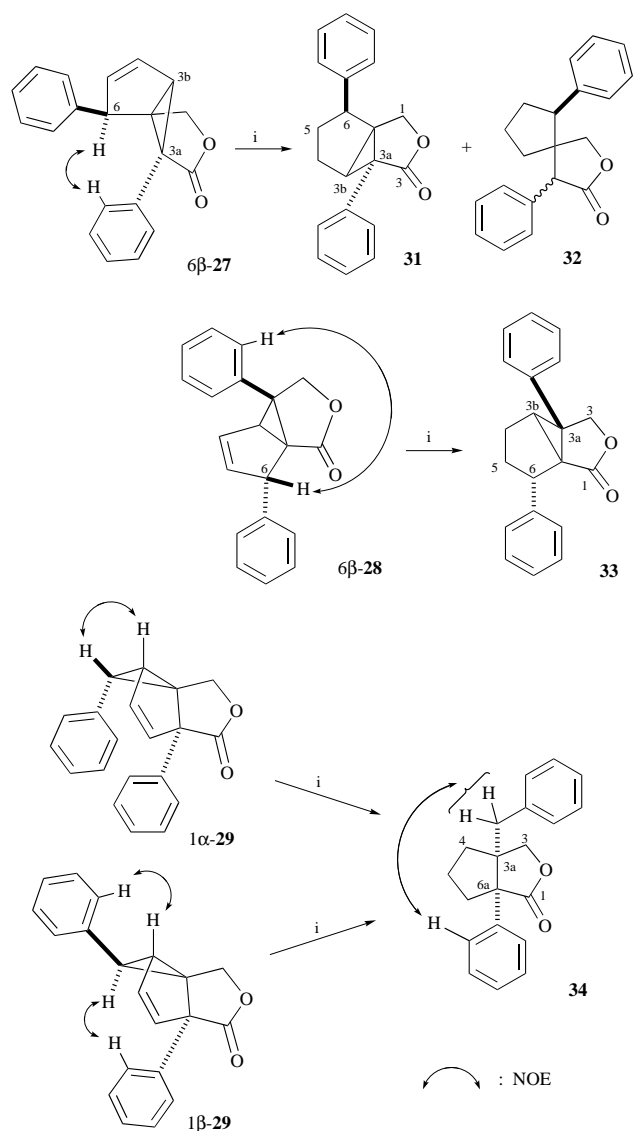
The stereochemistry of cyclohexa-1,4-diene **35**, 1,4-dihydronaphthalene **36** and 9,10-dihydroanthracene **37** and their derivatives has been the subject to a number of investigations and, after a long controversy, it now appears that compound **35** is planar, with substituent groups causing only modest derivation from the preferred conformation.<sup>11</sup> On the other hand, compound **37** was found to exist in a puckered conformation in the solid state with a folding angle (angle between the planes containing the benzene rings) of  $145^\circ$ . Because the solution NMR spectra at low temperature did not resolve individual pseudoaxial and pseudoequatorial protons in the central ring, it

was assumed that compound **37** exists as rapidly equilibrating boat conformations (**37A** and **37A'**) (Fig. 2). The tendency toward a boat conformation is reported to increase in the series **35** < **36** < **37**.

The solid-state structure of both diphenyl-substrates *cis*- and *trans*-**14** has been investigated in the present study by X-ray crystallography, and a planar structure has been established for both compounds *cis*- and *trans*-**14** (see Fig. 3 and Fig. 4). Molecular mechanics calculations also revealed that the planar structure is most stable for both *cis*- and *trans*-**14**.<sup>‡</sup> However, calculations indicated that difference of steric energy (*ca.* 6 kcal mol<sup>-1</sup>)<sup>§</sup> between the planar and the boat structure was small (see Fig. 5) with respect to both compounds *cis*- and *trans*-**14**.

<sup>‡</sup> Molecular mechanics calculations for these compounds employed the MM2 forcefield using Chem 3D Plus<sup>TM</sup>.

<sup>§</sup> The energy barrier in the chair-boat-chair interconversion has been reported to be near 11 kcal mol<sup>-1</sup> (ref. 11c).

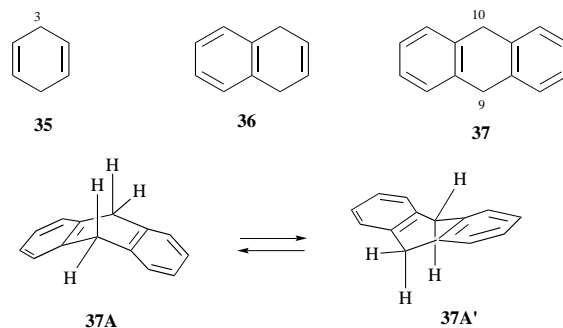


**Scheme 4** Reagents: i, H<sub>2</sub>, Pd-C

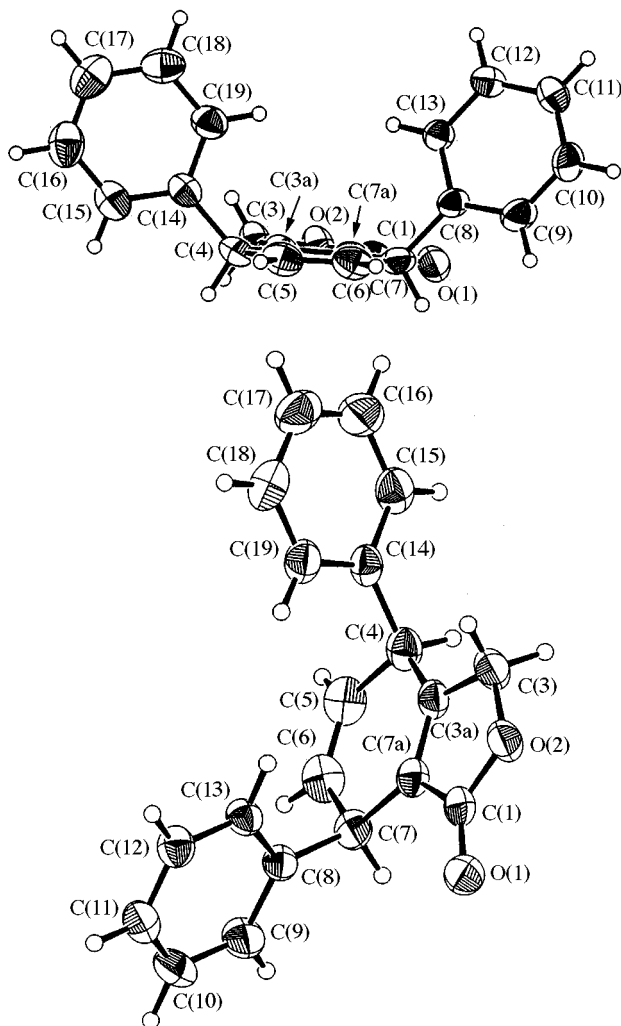
It was not hard for the two phenyl moieties in compound *cis*-**14** to exist in a bi-pseudoaxial configuration by facing each other in a parallel fashion (see Fig. 5); this behaviour was attributable to rapid boat-to-boat interconversion. The <sup>1</sup>H NMR spectrum of the *cis*-isomer *cis*-**14** also supported the rapid boat-to-boat interconversion or planar structure in solution, its homoallylic coupling constant having been in between ( $J_{4,7}$  7.0 Hz) those of the bi-pseudoaxial and bi-pseudo-equatorial protons in the systems.¶ Thus, previous speculation to the effect that a phenyl moiety in a pseudoaxial orientation would migrate has been strongly supported.

It is noteworthy that formation of compounds **27** is preferred to that of compounds **28** upon irradiation of both *cis*- and *trans*-diphenyl substituted substrates *cis*- and *trans*-**14**; a reverse selectivity of migration compared with compound **3** has been observed. The *cis*-isomer *cis*-**14** showed a stronger tendency, giving compounds **6a-27** and **6a-28** in a ratio of 28:5. A likely explanation for the preferential formation of compounds **27** over compound **28** would be as follows. In addition to the boat-to-boat inversion, rotation of the phenyl moiety around an axis formed between C-4 (or C-7) and an *ipso*-carbon of the phenyl

¶ The homoallylic coupling constant between two pseudoaxial protons in a substituted cyclohexa-1,4-diene system have been reported to be 12 Hz ( $J_{1,4^{cis}}$ ), while one between two pseudo-equatorial protons to be 2.6 Hz ( $J_{1,4^{eq}}$ ). In the planar structure, corresponding coupling constants have been reported to be 8.3 Hz ( $J_{1,4^{cis}}$ ) or 7.5 Hz ( $J_{1,4^{trans}}$ ) (ref. 11*d* and 11*f*).



**Fig. 2**



**Fig. 3** Molecular structure of compound *cis*-**14** determined by X-ray crystallography

moiety would have importance in bringing about photo-selectivity. Thus, the steric effect between one of the C-3 methylene hydrogens and the C-4 phenyl moiety might, through inhibition of the latter, rotate it insufficiently for the rearrangement (see Fig. 5). With respect to the *cis*-isomer *cis*-**14**, through-space interaction between the two phenyl substituents would exert an additional effect to inhibit the C-4 phenyl moiety, thus ensuring a favourable angle against the C(3a)=C(7a) double bond for the rearrangement, and resulting in regioselectivity in the photoreaction. Owing to the restricted rotation of the phenyl moieties in the boat conformation with pseudoaxial phenyl orientation, two curves (Type A and Type B in Fig. 5) were obtained in MM2 calculations which reflect the two possible relative geometries of the facing phenyl groups.

The preferential formation of compound **24** over compound **25** and also compounds **27** over compound **29** upon irradiation

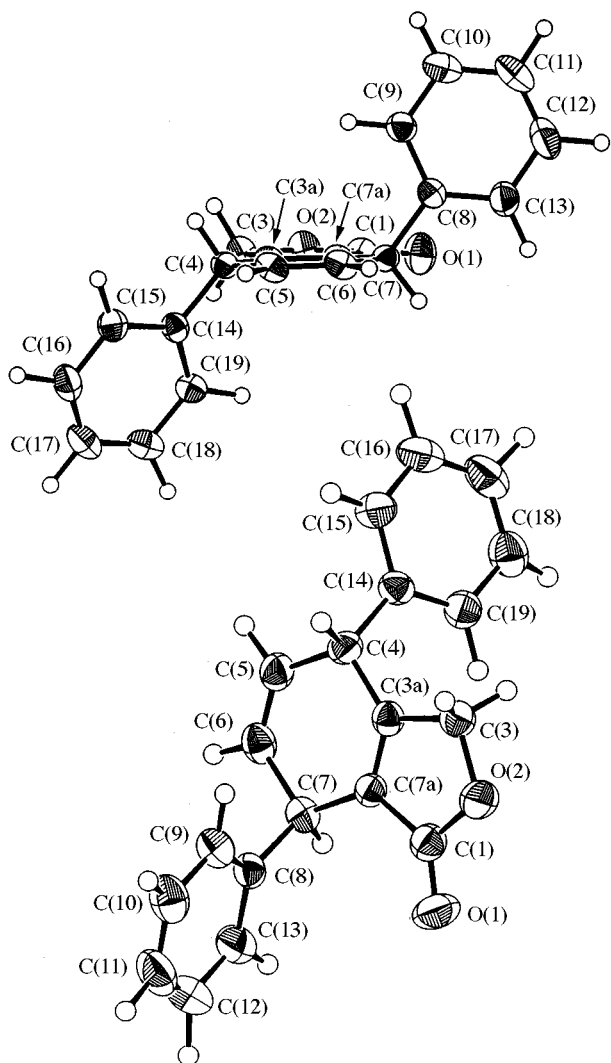


Fig. 4 Molecular structure of compound *trans*-14 determined by X-ray crystallography

of compounds **14** and **15**, respectively, is attributable to the reduced electron flow; route *a* leading to the formation of compounds **24** (or **27**) has been preferred to route *b* to compounds **25** (or **29**) as shown in Scheme 5.

In conclusion, both *cis*- and *trans*-4,7-disubstituted tetrahydroisobenzofuranones were found to be planar in the solid state, and the good agreement between the computation results and the X-ray data provided strong support for the validity of the calculations in predicting optimum structures for such compounds. The computation results also showed that these compounds are in rapid boat-to-boat interconversion in solution, and supported the previous prediction that the rearrangement would proceed *via* the boat conformation with a pseudoaxially oriented phenyl group. The origin of the characteristic regioselectivity observed especially in the photolysis of the *cis*-diphenyl substrate *cis*-14 has still to be resolved, but is likely to be rationalised in terms of a non-bonded steric effect between the two phenyl groups in the pseudoaxial orientation.

## Experimental

Mps were determined on a Yanagimoto MP-3S micro-melting 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  $^1\text{H}$ , 67.5 MHz  $^{13}\text{C}$ ) or a JEOL JNM-GSX 500 (500 MHz  $^1\text{H}$ , 125 MHz  $^{13}\text{C}$ ) spectrometer. Chemical shifts ( $\delta$ ) and coupling constants ( $J$ ) are given in ppm and Hz, respectively. All the NMR spectra were taken as  $\text{CDCl}_3$

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.

### Diels–Alder reaction of (1*E*,3*E*)-diphenylbuta-1,4-diene **16** with dimethyl acetylenedicarboxylate (DMAD)

A mixture of (1*E*,3*E*)-diphenylbuta-1,4-diene **16**<sup>6</sup> (5.75 g, 27.9 mmol) and DMAD (4.9 g, 34.5 mmol) was heated at 150 °C for 2.5 h. After being cooled, the residue was triturated with diethyl ether to give a pale yellow solid (9.6 g) which, on recrystallisation from methanol, gave dimethyl *cis*-3,6-diphenylcyclohexa-1,4-diene-1,2-dicarboxylate **17** (8.75 g, 90%) as prisms, mp 97–99 °C (lit.,<sup>6</sup> 97–98 °C). The spectral properties of compound **17** were in accord with those reported.<sup>6</sup>

### *cis*-4,7-Diphenyl-1,3,4,7-tetrahydroisobenzofuran-1,3-dione **18**

A mixture of the dimethyl ester **17** (8.3 g, 23.9 mmol), formic acid (80  $\text{cm}^3$ ), and perchloric acid (4  $\text{cm}^3$ ) was heated under reflux for 2 h. The reaction mixture was allowed to stand at room temperature, and deposited crystals were collected by filtration, and then washed with diisopropyl ether to give *title anhydride* **18** (6.8 g, 94%) as prisms, mp 157.5–158.5 °C (Found: C, 79.5; H, 4.8%;  $M^+$ , 302.0970.  $\text{C}_{20}\text{H}_{14}\text{O}_3$  requires C, 79.46; H, 4.67%;  $M$ , 302.0942);  $\nu_{\text{max}}(\text{CHCl}_3)/\text{cm}^{-1}$  1849, 1776, 1680 and 1633;  $\delta_{\text{H}}$  4.55–4.60 (2H, m), 5.98–6.01 (2H, m) and 7.29–7.44 (10H, m);  $\delta_{\text{C}}$  39.7 (d), 126.6 (d), 127.9 (d), 128.3 (d), 129.0 (d), 138.0 (s), 143.3 (s) and 163.3 (s);  $m/z$  302 ( $M^+$ , 99%), 257 (49), 225 (96), 152 (55) and 91 (100).

### Sodium boranuide reduction of the anhydride **18**

A solution of the anhydride **18** (6.3 g, 20.9 mmol) in THF (50  $\text{cm}^3$ ) was added dropwise to a stirred suspension of sodium boranuide (880 mg, 23.3 mmol) in THF (50  $\text{cm}^3$ ) at 0 °C, and the resulting mixture was stirred at 0 °C for 1.5 h. The mixture was then diluted with water (20  $\text{cm}^3$ ) and acidified with 10% hydrochloric acid to pH 2. After being stirred at room temperature for 2 h, the mixture was extracted with diethyl ether. The extract was washed successively with aq. sodium hydrogen carbonate and brine, and evaporated to give a pale yellow solid (6.2 g) which, on recrystallisation from a mixture of hexane and ethyl acetate, gave *cis*-4,7-diphenyl-1,3,4,7-tetrahydroisobenzofuran-1-one *cis*-14 (4.98 g, 83%) as needles, mp 120–122 °C (Found: C, 83.1; H, 5.7%;  $M^+$ , 288.1169.  $\text{C}_{20}\text{H}_{16}\text{O}_2$  requires C, 83.31; H, 5.59%;  $M$ , 288.1151);  $\lambda_{\text{max}}(\text{MeOH})/\text{nm}$  262 and 268 tailing to ca. 290 ( $\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$  1063 and 753);  $\nu_{\text{max}}(\text{CHCl}_3)/\text{cm}^{-1}$  1760, 1688 and 1633;  $m/z$  288 ( $M^+$ , 100%), 257 (87), 243 (79), 228 (57), 165 (44), 152 (43) and 91 (32).  $^1\text{H}$  and  $^{13}\text{C}$  NMR data of compound *cis*-14 are listed in Table 1.

### Isomerisation of the *cis*-diphenyl lactone *cis*-14

A mixture of compound *cis*-14 (2.09 g, 7.3 mmol), 1,4-diazabicyclo[2.2.2]octane (100 mg, 0.89 mmol) and methanol (50  $\text{cm}^3$ ) was stirred at room temperature for 21 h. The mixture was then poured into brine (100  $\text{cm}^3$ ) and extracted with diethyl ether. The extract was washed successively with 10% hydrochloric acid and brine, and then evaporated to give an oil (2.10 g) which, on column chromatography (hexane–ethyl acetate, 10:1), gave 4,7-diphenyl-1,3,6,7-tetrahydroisobenzofuran-1-one **19** (1.38 g, 66%), *trans*-4,7-diphenyl-1,3,4,7-tetrahydroisobenzofuran-1-one *trans*-14 (355 mg, 17%) and the starting material *cis*-14 (251 mg, 12%).

In a similar manner, compound *cis*-14 (2.00 g, 6.9 mmol) was treated with DABCO in methanol for 43 h to give compounds



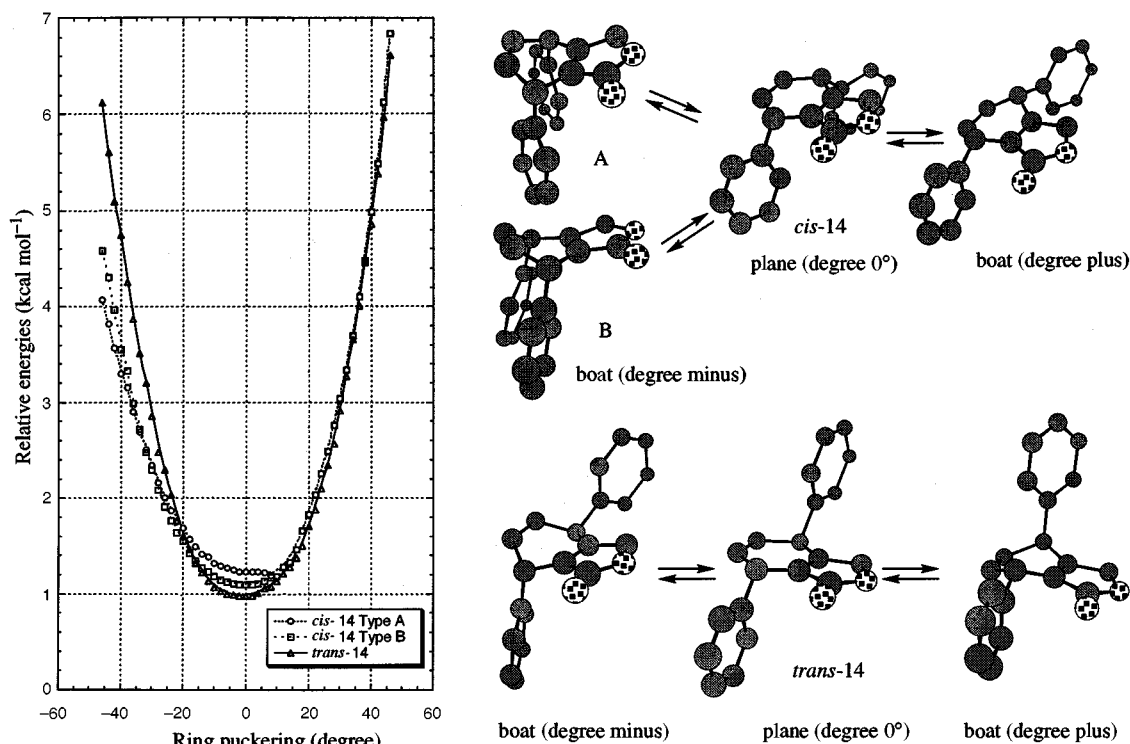
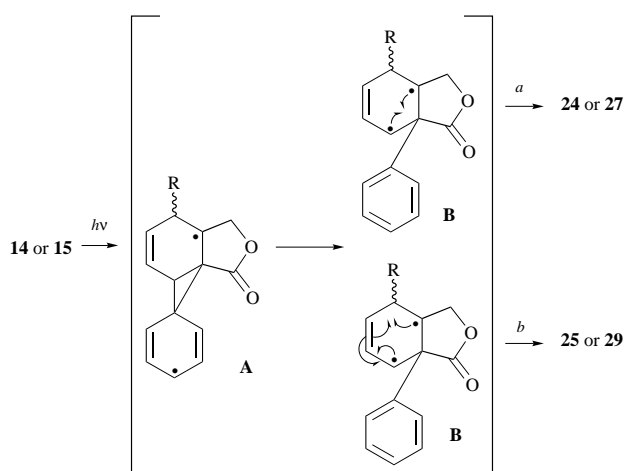


Fig. 5 MM2 calculations for compounds *cis*- and *trans*-14



Scheme 5

**19**, *trans*-14 and the starting material *cis*-14 in 80, 13 and 3% yields, respectively.

**1,3,6,7-Tetrahydroisobenzofuran-1-one 19**. Prisms, mp 142–145 °C (from hexane–diethyl ether) (Found: C, 83.4; H, 5.7%;  $M^+$ , 288.1148.  $C_{20}H_{16}O_2$  requires C, 83.31; H, 5.59%;  $M$ , 288.1151);  $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$  1748 and 1656;  $\delta_{\text{H}}$  2.95 (1H, ddd,  $J$  18.5, 6.0 and 3.0), 3.12 (1H, ddd,  $J$  18.5, 10.5 and 3.0), 3.99 (1H, br ddd,  $J$  10.5, 3.0 and 2.0), 4.86 (1H, dd,  $J$  17.5 and 2.0), 5.01 (1H, dd,  $J$  17.5 and 1.0), 6.28 (1H, dd,  $J$  6.0 and 3.0) and 7.23–7.45 (10H, m);  $\delta_{\text{C}}$  32.6 (t), 33.2 (d), 69.7 (t), 126.0 (s), 126.7 (d), 126.9 (d), 127.1 (d), 128.1 (d), 128.6 (d), 128.8 (d), 132.6 (d), 133.5 (s), 137.0 (s), 141.6 (s), 156.0 (s) and 172.9 (s);  $m/z$  288 ( $M^+$ , 100%), 243 (85), 228 (30), 165 (24) and 91 (39).

***trans*-1,3,4,7-Tetrahydroisobenzofuran-1-one *trans*-14**. Prisms, mp 150–152 °C (from hexane–ethyl acetate) (Found: C, 83.3; H, 5.8%;  $M^+$ , 288.1125);  $\lambda_{\max}(\text{MeOH})/\text{nm}$  262 and 268 tailing to ca. 290 ( $\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$  1595 and 1189);  $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$  1751, 1688 and 1633;  $m/z$  288 ( $M^+$ , 65%), 257 (10), 243 (100), 228 (35), 165 (82), 152 (78) and 91 (32).  $^1\text{H}$  and  $^{13}\text{C}$  NMR data for compound *trans*-14 are listed in Table 1.

#### Diels–Alder reaction of (1*E*,3*E*)- and (1*E*,3*Z*)-1-phenylpenta-1,3-diene (3*E*)- and (3*Z*)-20 with DMAD

Following a method similar to that used for the preparation of the diester **17**, a mixture of (1*E*,3*E*)- and (1*E*,3*Z*)-1-phenylpenta-1,3-diene (3*E*)- and (3*Z*)-**20**<sup>8</sup> ( $E/Z = \text{ca. } 5:1$ ; 4.8 g, 33.3 mmol) and DMAD (6.0 g, 42.2 mmol) was heated at 150 °C for 3 h. After removal of the excess of DMAD *in vacuo*, the residue was distilled at reduced pressure to give ca. 5.3:1 mixture of dimethyl *cis*- and *trans*-3-methyl-6-phenylcyclohexa-1,4-diene-1,2-dicarboxylate *cis*- and *trans*-**22** (7.7 g, 81%) as an oil.

In a similar manner, a mixture of the pentadienes (3*E*)- and (3*Z*)-**20** ( $E/Z = \text{ca. } 1:5.5$ ; 2.81 g, 19.5 mmol) afforded a mixture of the diesters *cis*- and *trans*-**22** ( $cis/trans = \text{ca. } 1:5$ ; 14.4 g, 79%). The ratio of compounds *cis*- and *trans*-**22** in the mixture was determined on the basis of the  $^1\text{H}$  NMR spectrum. Analytical samples of both diesters *cis*- and *trans*-**22** were obtained by means of column chromatography (hexane–ethyl acetate, 50:1).

**More polar isomer *cis*-22**. Oil, bp 150–151 °C (0.007 mmHg) (Found:  $M^+$ , 286.1220.  $C_{17}H_{18}O_4$  requires  $M$ , 286.1205);  $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$  1721, 1673 and 1635;  $\delta_{\text{H}}$  1.38 (3H, d,  $J$  7.0), 3.24 (1H, dqm,  $J$  7.0 and 7.0), 3.57 (3H, s), 3.80 (3H, s), 4.35–4.39 (1H, m), 5.69 (1H, dm,  $J$  10.0), 5.72 (1H, dm,  $J$  10.0) and 7.15–7.40 (5H, m);  $\delta_{\text{C}}$  21.6 (q), 32.7 (d), 44.0 (d), 51.8 (q), 52.1 (q), 126.4 (d), 126.8 (d), 127.5 (d), 128.1 (d), 128.5 (d), 133.5 (s), 139.5 (s), 141.3 (s), 167.4 (s) and 168.7 (s);  $m/z$  286 ( $M^+$ , 0.5%), 254 (24), 239 (100), 195 (27), 167 (26), 152 (24) and 91 (16).

**Less polar isomer *trans*-22**. Oil, bp 152–153 °C (0.008 mmHg) (Found:  $M^+$ , 286.1178);  $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$  1721, 1671 and 1637;  $\delta_{\text{H}}$  1.18 (3H, d,  $J$  7.0), 3.40 (1H, dqm,  $J$  7.0 and 7.0), 3.49 (3H, s), 3.78 (3H, s), 4.34–4.41 (1H, m), 5.68 (1H, dm,  $J$  10.0), 5.71 (1H, dm,  $J$  10.0) and 7.13–7.33 (5H, m);  $\delta_{\text{C}}$  20.2 (q), 31.7 (d), 43.3 (d), 51.7 (q), 52.0 (q), 126.1 (d), 127.0 (d), 127.4 (d), 128.3 (d), 128.5 (d), 133.8 (s), 138.0 (s), 141.4 (s), 167.5 (s) and 168.6 (s);  $m/z$  286 ( $M^+$ , 0.5%), 254 (67), 239 (100), 195 (71), 167 (55), 152 (50) and 91 (27).

#### *cis*- and *trans*-4-Methyl-7-phenyltetrahydroisobenzofuranones *cis*- and *trans*-15

Following a method similar to that used for the preparation of

the anhydride **18**, a mixture of *cis*- and *trans*-dimethyl esters *cis*- and *trans*-**22** (*cis/trans* = ca. 5.3:1; 7.4 g, 25.9 mmol) was treated with perchloric acid in formic acid. After removal of the solvent, the residue was diluted with diethyl ether (150 cm<sup>3</sup>), and the mixture was washed successively with aq. sodium hydrogen carbonate and brine, and then evaporated to give a mixture of the anhydrides, *cis*- and *trans*-4-methyl-7-phenyl-1,3,4,7-tetrahydroisobenzofuran-1,3-dione *cis*- and *trans*-**23**, as a pale brown oil (*cis/trans* = ca. 5.3:1; 15.5 g), which was used in the next step without purification.

A solution of the brown oil (5.5 g) in THF (10 cm<sup>3</sup>) was added to a suspension of sodium boranuide (958 mg, 25.3 mmol) in THF (20 cm<sup>3</sup>) at 0 °C, and the mixture was stirred at 0 °C for 1 h. Work-up in a manner similar to that used for the preparation of compound *cis*-**14** gave a pale brown oil (4.9 g), which was triturated with diethyl ether to give *cis*-4-methyl-7-phenyl-1,3,4,7-tetrahydroisobenzofuran-1-one *cis*-**15** (1.02 g, 17%) as a solid. Removal of the diethyl ether from the washings left a pale brown semi-solid (3.9 g), which was subjected to column chromatography (hexane–ethyl acetate, 10:1) to give compound *cis*-**15** (1.63 g, 28%); *cis*-7-methyl-4-phenyl-1,3,4,7-tetrahydroisobenzofuran-1-one *cis*-**21** (1.05 g, 18%), *trans*-4-methyl-7-phenyl-1,3,4,7-tetrahydroisobenzofuran-1-one *trans*-**15** (526 mg, 9%) and *trans*-7-methyl-4-phenyl-1,3,4,7-tetrahydroisobenzofuran-1-one *trans*-**21** (175 mg, 3%).

In a similar manner, a mixture of the dimethyl esters *cis*- and *trans*-**22** (*cis/trans* = ca. 1:5.1; 4.4 g, 15.4 mmol) afforded compounds *trans*-**15** (1.74 g, 50%), *trans*-**21** (592 mg, 17%), *cis*-**15** (310 mg, 9%) and *cis*-**21** (138 mg, 4%). <sup>1</sup>H and <sup>13</sup>C NMR data for compounds *cis*- and *trans*-**15** are listed in Table 1.

***cis*-Tetrahydroisobenzofuranone *cis*-15.** Leaflets, mp 115–117 °C (from EtOH) (Found: C, 79.4; H, 6.2%; M<sup>+</sup>, 226.1015). C<sub>15</sub>H<sub>14</sub>O<sub>2</sub> requires C, 79.62; H, 6.24%; M, 226.0994; λ<sub>max</sub>(MeOH)/nm 261 and 268 tailing to ca. 290 (ε/dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup> 429 and 278); ν<sub>max</sub>(CHCl<sub>3</sub>)/cm<sup>-1</sup> 1757, 1687 and 1636; m/z 226 (M<sup>+</sup>, 49%), 211 (100), 181 (30), 167 (48), 152 (25) and 91 (13).

***trans*-Tetrahydroisobenzofuranone *trans*-15.** Needles, mp 80–82 °C (from hexane–diethyl ether) (Found: C, 79.6; H, 6.4%; M<sup>+</sup>, 226.1015); λ<sub>max</sub>(MeOH)/nm 261 and 268 tailing to ca. 290 (ε/dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup> 463 and 301); ν<sub>max</sub>(CHCl<sub>3</sub>)/cm<sup>-1</sup> 1758, 1685 and 1635; m/z 226 (M<sup>+</sup>, 52%), 211 (100), 181 (33), 167 (53), 152 (28) and 91 (18).

***cis*-Tetrahydroisobenzofuranone *cis*-21.** Needles, mp 92–94 °C (from hexane–ethyl acetate) (Found: C, 79.5; H, 6.4%; M<sup>+</sup>, 226.1001); λ<sub>max</sub>(MeOH)/nm 261 and 268 tailing to ca. 290 (ε/dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup> 565 and 376); ν<sub>max</sub>(CHCl<sub>3</sub>)/cm<sup>-1</sup> 1757, 1691 and 1636; δ<sub>H</sub> 1.41 (3H, d, J 7.0), 3.13–3.28 (1H, br m), 4.26 (1H, dm, J 7.0), 4.41 (1H, ddd, J 17.0, 2.0, 0.5), 4.65 (1H, ddd, J 17.0, 2.5, 1.0), 5.74 (1H, ddd, J 10.0, 3.0, 2.0), 5.90 (1H, ddd, J 10.0, 3.5, 2.0), 7.13–7.19 (2H, m) and 7.25–7.40 (3H, m); δ<sub>C</sub> 19.8 (q), 27.8 (d), 42.7 (d), 70.5 (t), 125.1 (d), 127.6 (d), 127.8 (d), 128.0 (s), 129.2 (d), 130.8 (d), 140.1 (s), 159.2 (s) and 173.1 (s); m/z 226 (M<sup>+</sup>, 70%), 211 (13), 181 (80), 167 (100), 152 (48) and 91 (38).

***trans*-Tetrahydroisobenzofuranone *trans*-21.** Needles, mp 56–57 °C (from hexane–diethyl ether) (Found: C, 79.8; H, 6.3%; M<sup>+</sup>, 226.1006); λ<sub>max</sub>(MeOH)/nm 261 and 268 tailing to ca. 290 (ε/dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup> 552 and 353); ν<sub>max</sub>(CHCl<sub>3</sub>)/cm<sup>-1</sup> 1756, 1686 and 1634; δ<sub>H</sub> 1.34 (3H, d, J 7.0), 3.16–3.31 (1H, br m), 4.26 (1H, br m), 4.35 (1H, ddd, J 17.0, 2.5, 0.5), 4.65 (1H, ddd, J 17.0, 1.5, 1.5), 5.75 (1H, ddd, J 10.0, 3.0, 2.0), 5.91 (1H, ddd, J 10.0, 3.0, 2.0), 7.08–7.17 (2H, m) and 7.23–7.38 (3H, m); δ<sub>C</sub> 19.3 (q), 27.7 (d), 42.4 (d), 70.4 (t), 125.1 (d), 127.6 (d), 127.8 (d), 127.9 (s), 129.1 (d), 130.7 (d), 140.5 (s), 159.4 (s) and 173.0 (s); m/z 226 (M<sup>+</sup>, 73%), 211 (13), 181 (74), 167 (100), 152 (44) and 91 (30).

#### Photolysis of compounds **14** and **15**

**General procedure.** All the irradiations, except those in a Pyrex test tube, were carried out to a solution of the reactant (100 mg) in methanol (200 cm<sup>3</sup>) or acetone (200 cm<sup>3</sup>) 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. Solutions were degassed by a 30-min sonication and a subsequent 30-min argon purge prior to photolysis. All the irradiations were monitored by <sup>1</sup>H NMR measurements, and primary formation of the di-π-methane rearrangement products was detected at the beginning of the irradiation. Reactions were terminated before the reaction mixture became too complex to be fractionalised (time and product distribution are given in Tables 2 and 3 in Scheme 3). Irradiation was repeated three times for every reactant, and the product ratios of compounds **24–30** were satisfactorily reproducible. Products **24–30** were isolated by column chromatography of the residue left after removal of the solvent using hexane–ethyl acetate (10:1) as an eluent. <sup>1</sup>H and <sup>13</sup>C NMR data of the rearrangement products **24**, **25**, **27**, **28** and **29** are listed in Table 4 and 5.

#### Photolysis of the *trans*-methyl phenyl lactone *trans*-15 in methanol

Three rearrangement products, 6β-methyl-3αa-phenyl-3,3a,3b,6-tetrahydro-1H-cyclopenta[1,3]cyclopropa[1,2-c]furan-3-one 6β-**24**, 1α-methyl- and 1β-methyl-3αa-phenyl-1,1a,3a,4-tetrahydro-6H-cyclopropa[1,5]cyclopenta[1,2-c]furan-4-one 1α- and 1β-**25** and a dehydrogenated product, 4-methyl-7-phenyl-1,3-dihydroisobenzofuran-1-one **26**, were obtained together with recovery of a small amount of the starting material *trans*-**15**.

**6β-Tetrahydrocyclopropacyclopentafuranone 6β-24.** Prisms, mp 75–76 °C (from hexane–diethyl ether) (Found: C, 79.7; H, 6.3%; M<sup>+</sup>, 226.0968). C<sub>15</sub>H<sub>14</sub>O<sub>2</sub> requires C, 79.62; H, 6.24%; M, 226.0994; ν<sub>max</sub>(CHCl<sub>3</sub>)/cm<sup>-1</sup> 1766; m/z 226 (M<sup>+</sup>, 31%), 181 (78), 167 (100), 152 (42), 115 (24) and 91 (28).

**1α-Tetrahydrocyclopropacyclopentafuranone 1α-25.** Plates, mp 94–95 °C (from hexane–ethyl acetate) (Found: M<sup>+</sup>, 226.1012); ν<sub>max</sub>(CHCl<sub>3</sub>)/cm<sup>-1</sup> 1762; m/z 226 (M<sup>+</sup>, 10%), 181 (50), 167 (100), 152 (41), 115 (16) and 91 (10).

**1β-Tetrahydrocyclopropacyclopentafuranone 1β-25.** Prisms, mp 156–157 °C (from hexane–ethyl acetate) (Found: M<sup>+</sup>, 226.1004); ν<sub>max</sub>(CHCl<sub>3</sub>)/cm<sup>-1</sup> 1771; m/z 226 (M<sup>+</sup>, 15%), 181 (73), 167 (100), 152 (44), 115 (19) and 91 (16).

**Dihydroisobenzofuranone 26.** Needles, mp 118–119 °C (from EtOH) (Found: M<sup>+</sup>, 224.0812). C<sub>15</sub>H<sub>12</sub>O<sub>2</sub> requires M, 224.0837; ν<sub>max</sub>(CHCl<sub>3</sub>)/cm<sup>-1</sup> 1763; δ<sub>H</sub> 2.39 (3H, s), 5.24 (2H, s) and 7.34–7.58 (7H, m); δ<sub>C</sub> 17.0 (q), 67.8 (t), 121.3 (s), 127.8 (d), 128.0 (d), 129.4 (d), 130.9 (d), 131.0 (s), 134.5 (d), 136.4 (s), 140.1 (s), 146.6 (s) and 170.2 (s); m/z 224 (M<sup>+</sup>, 95%), 195 (100), 165 (33) and 152 (29).

#### Photolysis of *cis*-methyl phenyl lactone *cis*-15 in methanol

Three rearrangement products, 6α-methyl-3αa-phenyl-3,3a,3b,6-tetrahydro-1H-cyclopenta[1,3]cyclopropa[1,2-c]furan-3-one 6α-**24**, tetrahydrocyclopropacyclopentafuranones 1α- and 1β-**25** and a dehydrogenated product **26** were obtained together with a recovery of a small amount of the starting material *cis*-**15**. The physical and spectral properties of compounds 1α-**25**, 1β-**25** and **26** were in accord with those of authentic specimens obtained by irradiation of the *trans*-counterpart *trans*-**15**.

**6α-Tetrahydrocyclopropacyclopentafuranone 6α-24.** Prisms, mp 159–160 °C (from EtOH) (Found: C, 79.8; H, 6.3%; M<sup>+</sup>, 226.1012). C<sub>15</sub>H<sub>14</sub>O<sub>2</sub> requires C, 79.62; H, 6.24%; M, 226.0994; ν<sub>max</sub>(CHCl<sub>3</sub>)/cm<sup>-1</sup> 1762; m/z 226 (M<sup>+</sup>, 28%), 181 (72), 167 (100), 152 (43), 115 (23) and 91 (30).

#### Photolysis of the *trans*-diphenyl lactone *trans*-14 in methanol

Four rearrangement products, 3αa,6β-diphenyl-3,3a,3b,6-tetrahydro-1H-cyclopenta[1,3]cyclopropa[1,2-c]furan-3-one 6β-**27**, 3αa,6β-diphenyl-3,3a,3b,6-tetrahydro-1H-cyclopenta[1,3]-cyclopropa[1,2-c]furan-1-one 6β-**28**, 1α,3αa- and 1β,3αa-diphenyl-1,1a,3a,4-tetrahydro-6H-cyclopropa[1,5]cyclopenta[1,2-c]furan-4-one 1α- and 1β-**29** and a dehydrogenated product,

4,7-diphenyl-1,3-dihydroisobenzofuran-1-one **30**, were obtained together with recovery of a small amount of the starting material *trans*-**14**.

**3 $\alpha$ ,6 $\beta$ -Tetrahydrocyclopentacyclopropafuran-3-one 6 $\beta$ -27.** Prisms, mp 138–139.5 °C (from hexane–ethyl acetate) (Found: C, 83.4; H, 5.6%; M<sup>+</sup>, 288.1137. C<sub>20</sub>H<sub>16</sub>O<sub>2</sub> requires C, 83.31; H, 5.59%; M, 288.1151);  $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$  1762;  $m/z$  288 (M<sup>+</sup>, 100%), 243 (62), 228 (42), 165 (41), 152 (34), 115 (42) and 91 (59).

**3 $\alpha$ ,6 $\beta$ -Tetrahydrocyclopentacyclopropafuran-1-one 6 $\beta$ -28.** Needles, mp 198–199 °C (from hexane–ethyl acetate) (Found: M<sup>+</sup>, 288.1173);  $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$  1763;  $m/z$  288 (M<sup>+</sup>, 88%), 243 (73), 228 (42), 215 (45), 165 (44), 152 (31), 115 (45), 105 (100) and 91 (41).

**1 $\alpha$ ,3 $\alpha$ -Tetrahydrocyclopropacyclopentafuranone 1 $\alpha$ -29.** Needles, mp 139.5–140 °C (from hexane–ethyl acetate) (Found: M<sup>+</sup>, 288.1176);  $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$  1764;  $m/z$  288 (M<sup>+</sup>, 26%), 243 (100), 229 (56), 165 (55), 152 (26), 115 (25) and 91 (19).

**1 $\beta$ ,3 $\alpha$ -Tetrahydrocyclopropacyclopentafuranone 1 $\beta$ -29.** Prisms, mp 110–112 °C (from hexane–ethyl acetate) (Found: M<sup>+</sup>, 288.1124);  $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$  1763;  $m/z$  288 (M<sup>+</sup>, 38%), 243 (100), 229 (57), 165 (49), 152 (22), 115 (25) and 91 (13).

**Dihydroisobenzofuranone 30.** Prisms, mp 173–175 °C (from EtOH) (Found: C, 83.4; H, 5.0%; M<sup>+</sup>, 286.0984. C<sub>20</sub>H<sub>14</sub>O<sub>2</sub> requires C, 83.30; H, 4.93%; M, 286.0994);  $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$  1764;  $\delta_{\text{H}}$  5.38 (2H, s) and 7.38–7.78 (12H, m);  $\delta_{\text{C}}$  68.4 (t), 122.2 (s), 127.8 (d), 127.9 (d), 128.3 (d), 128.4 (d), 129.1 (d), 129.5 (d), 131.5 (d), 133.5 (d), 135.7 (s), 136.2 (s), 137.4 (s), 141.6 (s), 145.4 (s) and 169.8 (s);  $m/z$  286 (M<sup>+</sup>, 99%), 257 (100) and 228 (27).

#### Photolysis of the *cis*-diphenyl lactone *cis*-**14** in methanol

Four rearrangement products, 3 $\alpha$ ,6 $\alpha$ -diphenyl-3,3 $\alpha$ ,3 $\beta$ ,6-tetrahydro-1H-cyclopenta[1,3]cyclopropa[1,2-c]furan-3-one 6 $\alpha$ -27, 3 $\alpha$ ,6 $\alpha$ -diphenyl-3,3 $\alpha$ ,3 $\beta$ ,6-tetrahydro-1H-cyclopenta[1,3]cyclopropa[1,2-c]furan-1-one 6 $\alpha$ -28, the tetrahydrocyclopropacyclopentafuranones 1 $\alpha$ - and 1 $\beta$ -29, and a dehydrogenated product **30** were obtained together with recovery of a small amount of the starting material *cis*-**14**. The physical and spectral properties of compounds 1 $\alpha$ -29, 1 $\beta$ -29 and **30** were in accord with those of authentic specimens obtained by irradiation of the *trans*-counterpart *trans*-**14**.

**3 $\alpha$ ,6 $\alpha$ -Tetrahydrocyclopentacyclopropafuran-3-one 6 $\alpha$ -27.** Needles, mp 144–145 °C (from hexane–ethyl acetate) (Found: C, 83.5; H, 5.7%; M<sup>+</sup>, 288.1176. C<sub>20</sub>H<sub>16</sub>O<sub>2</sub> requires C, 83.31; H, 5.59%; M, 288.1151);  $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$  1763;  $m/z$  288 (M<sup>+</sup>, 100%), 243 (54), 228 (34), 165 (27), 152 (18), 115 (21) and 91 (27).

**3 $\alpha$ ,6 $\alpha$ -Tetrahydrocyclopentacyclopropafuran-1-one 6 $\alpha$ -28.** Prisms, mp 107.5–108.5 °C (from hexane–diethyl ether) (Found: C, 83.6; H, 5.7%; M<sup>+</sup>, 288.1148);  $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$  1762;  $m/z$  288 (M<sup>+</sup>, 100%), 243 (80), 228 (37), 215 (43), 165 (43), 152 (26), 115 (37), 105 (81) and 91 (30).

#### Photolysis of compounds **14** and **15** in acetone

Compounds **14** and **15** in acetone were photolysed under the conditions described in the general experimental section, and the results are listed in Tables 2 and 3 in Scheme 3.

#### Photolysis of the tetrahydrocyclopropacyclopentafuranones 1 $\alpha$ -25, 1 $\beta$ -25, 1 $\alpha$ -29 and 1 $\beta$ -29 in acetone

A solution of compound 1 $\alpha$ -25 (5.0 mg, 0.022 mmol) in degassed acetone (1.5 cm<sup>3</sup>) in a Pyrex test tube was irradiated for 9 h. Removal of the solvent left a pale yellow oil (5.0 mg) which was a 5:1:2.1:5 mixture of compounds 1 $\alpha$ -24, 1 $\beta$ -24 and 1 $\beta$ -25 and the starting material 1 $\alpha$ -25 (by <sup>1</sup>H NMR spectroscopy).

In a similar manner, compound 1 $\beta$ -25 (5.0 mg, 0.022 mmol) afforded a 2.2:1.2:2.7:1 mixture of compounds 1 $\alpha$ -24, 1 $\beta$ -24 and 1 $\alpha$ -25 and the starting material 1 $\beta$ -25 (by <sup>1</sup>H NMR spectroscopy).

In a similar manner compound 1 $\alpha$ -29 (5.0 mg, 0.017 mmol) afforded a 1:1.6:3.6 mixture of compounds 1 $\alpha$ -27 and 1 $\beta$ -29 and the starting material 1 $\alpha$ -29 (by <sup>1</sup>H NMR spectroscopy). Formation of a trace amount of compound 1 $\beta$ -27 was detected on the basis of the <sup>1</sup>H NMR spectrum.

In a similar manner, compound 1 $\beta$ -29 (5.0 mg, 0.017 mmol) afforded a 1:3.7:1.7 mixture of compounds 1 $\alpha$ -27 and 1 $\alpha$ -29 and the starting material 1 $\beta$ -29 (by <sup>1</sup>H NMR spectroscopy). Formation of a trace amount of compound 1 $\beta$ -27 was detected on the evidence of the <sup>1</sup>H NMR spectrum.

#### Catalytic hydrogenation of the photoproducts 6 $\beta$ -27, 6 $\beta$ -28, 1 $\alpha$ -29 and 1 $\beta$ -29

A suspension of 5% palladium-on-carbon (20 mg) in ethanol (2 cm<sup>3</sup>) was pre-equilibrated with hydrogen. To the suspension was added a solution of compound 6 $\beta$ -27 (24 mg, 0.083 mmol) in ethanol (4 cm<sup>3</sup>), and hydrogenation was continued at room temperature and atmospheric pressure for 5 h. The catalyst was filtered off, and the filtrate was evaporated to give quantitatively a solid which, on PTLC (hexane–acetone, 50:1), gave 3 $\alpha$ ,6 $\beta$ -diphenyl-3,3 $\alpha$ ,3 $\beta$ ,4,5,6-hexahydro-1H-cyclopenta[1,3]cyclopropa[1,2-c]furan-3-one **31** (21.5 mg, 89%) and 2,3'-diphenylspirocyclopentane-1,4'-tetrahydrofuran-2'-one **32** (1.3 mg, 5%).

**Hexahydrocyclopentacyclopropafuran-3-one 31.** Prisms, mp 149.5–150 °C (from EtOH) (M<sup>+</sup>, 290.1280. C<sub>20</sub>H<sub>18</sub>O<sub>2</sub> requires M, 290.1307);  $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$  1760;  $\delta_{\text{H}}$  0.92 (1H, dddd, J 14.0, 10.5, 9.0 and 9.0), 1.50 (1H, dd, J 14.0 and 9.5), 1.95 (1H, dd, J 14.0 and 9.0), 2.19 (1H, d, J 5.0), 2.39 (1H, dddd, J 14.0, 10.5, 9.5 and 5.0), 3.44 (1H, d, J 9.0), 4.09 (1H, d, J 10.0), 4.27 (1H, br d, J 10.0), 7.21–7.29 (3H, m) and 7.32–7.45 (7H, m);  $\delta_{\text{C}}$  25.9 (t), 31.8 (t), 34.2 (d), 39.4 (s), 45.2 (d), 47.5 (s), 69.2 (t), 127.0 (d), 127.1 (d), 128.3 (d), 128.98 (d), 129.04 (d), 130.0 (d), 131.3 (s), 142.9 (s) and 176.2 (s);  $m/z$  290 (M<sup>+</sup>, 68%), 245 (95), 142 (73), 128 (59), 115 (71), 104 (100) and 91 (67).

**Spirotetrahydrofuranone 32.** Needles, mp 65–67 °C (from diethyl ether) (M<sup>+</sup>, 292.1438. C<sub>20</sub>H<sub>20</sub>O<sub>2</sub> requires M, 292.14643);  $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$  1758;  $\delta_{\text{H}}$  1.77–2.09 (6H, m), 2.80 (1H, dd, J 8.5 and 5.5), 3.52 (1H, s), 3.72 (1H, d, J 10.0), 4.00 (1H, d, J 10.0), 6.71–6.74 (2H, m), 7.13–7.20 (5H, m) and 7.36–7.44 (3H, m);  $\delta_{\text{C}}$  23.7 (t), 33.1 (t), 39.5 (t), 47.2 (d), 55.8 (s), 58.3 (d), 75.2 (t), 126.6 (d), 127.9 (d), 128.0 (d), 128.4 (d), 129.0 (d), 129.1 (d), 134.7 (s), 142.4 (s) and 177.6 (s);  $m/z$  292 (M<sup>+</sup>, 3%), 157 (100), 129 (53), 115 (39) and 91 (70).

In a similar manner, compound 6 $\beta$ -28 (14.0 mg, 0.049 mmol) afforded quantitatively a solid which, on recrystallisation from ethanol, gave 3 $\alpha$ ,6 $\alpha$ -diphenyl-3,3 $\alpha$ ,3 $\beta$ ,4,5,6-hexahydro-1H-cyclopenta[1,3]cyclopropa[1,2-c]furan-1-one **33** (12.9 mg, 92%) as prisms, mp 218–219.5 °C (M<sup>+</sup>, 290.1285. C<sub>20</sub>H<sub>18</sub>O<sub>2</sub> requires M, 290.1307);  $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$  1761;  $\delta_{\text{H}}$  0.79–0.89 (1H, m), 1.30 (1H, dd-like, J 14.0 and 8.5), 1.95–2.01 (1H, m), 2.32–2.42 (1H, m), 2.38 (1H, br s-like), 3.42 (1H, d, J 8.0), 4.15 (1H, d, J 9.5), 4.33 (1H, br d, J 9.5) and 7.21–7.46 (10H, m);  $\delta_{\text{C}}$  24.5 (t), 33.5 (t), 37.8 (d), 41.4 (s), 42.7 (s), 43.6 (d), 76.8 (t), 126.5 (d), 127.3 (d), 128.26 (d), 128.29 (d), 128.7 (d), 129.4 (d), 135.0 (s), 142.9 (s) and 173.7 (s);  $m/z$  290 (M<sup>+</sup>, 3%), 245 (36), 142 (11), 128 (13), 115 (12), 104 (100) and 91 (13).

In a similar manner, compound 1 $\alpha$ -29 (12.0 mg, 0.04 mmol) afforded quantitatively a solid which, on recrystallisation from ethanol, gave 3 $\alpha$ -benzyl-6 $\alpha$ -phenylhexahydro-1H-cyclopenta[c]furan-1-one **34** (10.9 mg, 90%) as needles, mp 94–95 °C (M<sup>+</sup>, 292.1481. C<sub>20</sub>H<sub>20</sub>O<sub>2</sub> requires M, 292.1463);  $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$  1758;  $\delta_{\text{H}}$  1.63–1.77 (2H, m), 1.92–2.01 (1H, m), 2.08–2.17 (1H, m), 2.11 (1H, d, J 13.5), 2.27 (1H, d, J 13.5), 2.52 (2H, d, J 8.5 and 5.5), 4.02 (1H, d, J 9.5), 4.36 (1H, br d, J 9.5), 6.97–7.01 (2H, m) and 7.16–7.43 (8H, m);  $\delta_{\text{C}}$  23.8 (t), 35.8 (t), 38.2 (t), 42.3 (t), 53.9 (s), 64.1 (s), 76.5 (t), 126.7 (d), 127.3 (d), 127.7 (d), 128.4 (d), 128.8 (d), 129.3 (d), 136.8 (s), 137.3 (s) and 182.0 (s);  $m/z$  292 (M<sup>+</sup>, 13%), 201 (12), 157 (97), 129 (98) and 91 (100).

In a similar manner, compound 1 $\beta$ -29 (13 mg, 0.05 mmol) afforded needles (11.6 mg, 89%), the physical and spectral

properties of which were identical with those of an authentic specimen of compound **34** obtained from compound **1a-29**.

### X-Ray crystallography

Data for both compounds *cis*- and *trans*-**14** were measured on a Rigaku AFC5R diffractometer with graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.710\ 69\ \text{\AA}$ ). Their structures were solved by direct methods (MITHRIL).<sup>12</sup> Full-matrix least-squares refinement was employed with anisotropic thermal parameters for all non-hydrogen atoms. All computations for the structure determination were carried out on a VAX station 3200 using the crystallographic program package TEXSAN.<sup>13</sup> ORTEP drawings of compounds *cis*- and *trans*-**14** are shown in Figs. 2 and 3, respectively. Tables of atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC).||

**Crystal data for the *cis*-diphenyl lactone *cis*-**14**.** C<sub>20</sub>H<sub>16</sub>O<sub>2</sub>,  $M = 288.35$ , monoclinic, space group  $P2_1/c$ ,  $a = 9.128(7)$ ,  $b = 14.800(2)$ ,  $c = 11.803(2)\ \text{\AA}$ ,  $\alpha = 90.00^\circ$ ,  $\beta = 106.52(2)^\circ$ ,  $\gamma = 90.00^\circ$ ,  $V = 1529(1)\ \text{\AA}^3$ ,  $Z = 4$ ,  $\mu(\text{Mo-K}\alpha) = 0.74\ \text{cm}^{-1}$ ,  $F(000) = 608$ ,  $D_c = 1.253\ \text{g cm}^{-3}$ , crystal dimensions:  $0.10 \times 0.10 \times 0.20\ \text{mm}$ . A total of 3882 reflections (3664 unique) were collected using the  $\omega$ - $2\theta$  scan technique to a maximum  $2\theta$  value of  $55^\circ$  and 1468 reflections with  $I > 3\sigma(I)$  were used in the structure determination. Final  $R$  and  $R_w$  values were 0.039 and 0.043, respectively. The maximum and minimum peaks in the difference map were 0.11 and  $-0.12\ \text{e \AA}^{-3}$ , respectively.

**Crystal data for the *trans*-diphenyl lactone *trans*-**14**.** C<sub>20</sub>H<sub>16</sub>O<sub>2</sub>,  $M = 288.35$ , triclinic, space group  $P1$ ,  $a = 8.830(1)$ ,  $b = 14.071(2)$ ,  $c = 6.2948(2)\ \text{\AA}$ ,  $\alpha = 102.927(8)^\circ$ ,  $\beta = 97.01(1)^\circ$ ,  $\gamma = 102.506(9)^\circ$ ,  $V = 732.1(2)\ \text{\AA}^3$ ,  $Z = 2$ ,  $\mu(\text{Mo-K}\alpha) = 0.78\ \text{cm}^{-1}$ ,  $F(000) = 304$ ,  $D_c = 1.308\ \text{g cm}^{-3}$ , crystal dimensions:  $0.20 \times 0.20 \times 0.30\ \text{mm}$ . A total of 3586 reflections (3366 unique) were collected using the  $\omega$ - $2\theta$  scan technique to a maximum  $2\theta$  value of  $55^\circ$ , and 1902 reflections with  $I > 3\sigma(I)$  were used in the structure determination. Final  $R$  and  $R_w$  values were 0.044 and 0.049, respectively. The maximum and minimum peaks in the difference map were 0.17 and  $-0.17\ \text{e \AA}^{-3}$ , respectively.

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