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Photoisomerisation of (*E*)-Iodoalkylidene Lactones A Route to (Z)-Iodoalkylidene Lactones

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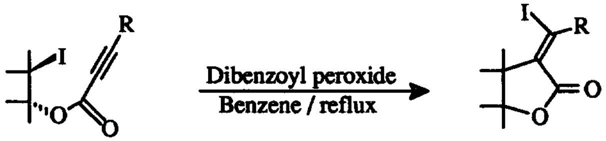
ABSTRACT - *Photochemically induced free-radical cyclisation of iodo acetylenic esters provides low yields of mixtures from which both (E)- and (Z)-iodoalkylidene lactones may be isolated. However, photoisomerisation of (E)-iodolkylidene lactones, which have previously been obtained in good yields by dibenzoyl peroxide induced cyclisation of iodo acetylenic esters, provides (E)/(Z)-mixtures from which the previously inaccessible (Z)-isomers may be isolated by chromatography. Also reported is a collection of IR, UV and NMR spectral data, all of which provide useful information relating to the stereochemistry of the iodoalkylidene lactones. A comparison of the crystal structures of the (E)- and (Z)-isomers of a trimethylsilyl iodomethylene lactone is also included.*

INTRODUCTION

We have recently described a conversion of alkenes into iodoalkylidene lactones which have the (*E*) geometry in almost all cases[1]. The key step in this route is a chemically induced free-radical cyclisation of iodo acetylenic esters (Scheme 1) which may be derived from alkenes by addition of the appropriate acetylenic acid in the presence of N-iodosuccinimide. To date only one other route to an iodoalkylidene lactone has been reported[2]. In that instance, palladium catalysed cyclisation of 4-iodo-2-butenyl propynoate gave moderate yields of a mixture of (*E*)- and (Z)-iodomethylene lactones which was not separated.



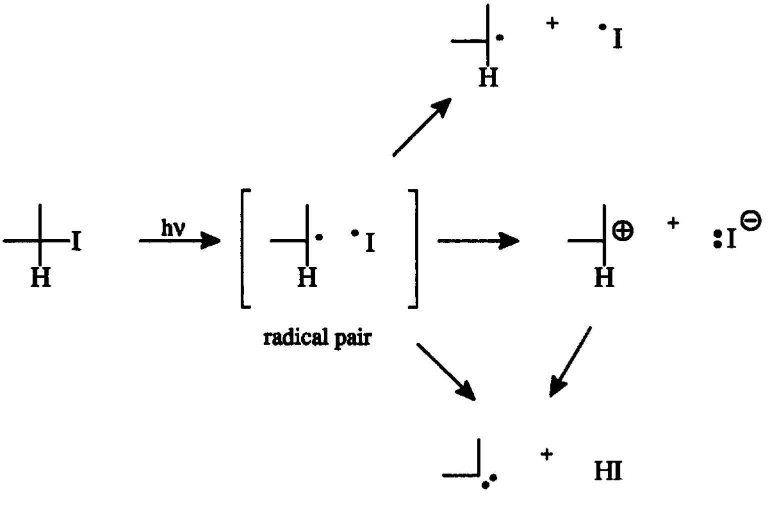
Scheme 1

We have also demonstrated that photochemical initiation achieves the same end, but in a less stereospecific manner[3]. However, this opens up access to the (Z)-iodoalkylidene lactones. This paper describes these photochemical transformations in more detail, and elaborates a more practical source of the (Z)-isomers through photochemical isomerisation of their (*E*)-counterparts.

PHOTOCHEMICAL CYCLISATION

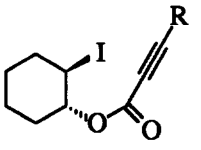
Irradiation of an alkyl iodide results in the promotion of an n electron into the σ^* orbital. This transition occurs at an energy of approximately 380 kJ mol^{-1} which exceeds the carbon iodine bond energy (*c.a.* 210 kJ mol^{-1}). Thus, light induced cleavage can occur and ground state reactions of the resulting radicals ensue. Although the bond scission is highly efficient, overall quantum yields are low as a result of rapid radical recombination[4]. Nonetheless, the process is useful in organic synthesis.

The photochemical reactions of alkyl iodides, both in solution and in the gas phase, were initially interpreted solely in terms of radical intermediates[4]. However, there is strong evidence in many cases for subsequent formation of either carbocationic or carbenic intermediates[5,6]. The carbocations appear to arise by electron transfer within the initially formed radical pair, while carbenes may result from either hydrogen atom abstraction from the radical by an iodine radical, or by proton removal from the cationic centre (Scheme 2). In general, carbocationic pathways are more common than carbenic[5].

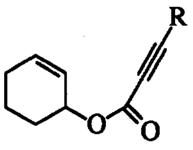


Scheme 2

Initial attempts to procure alkylidene lactones photochemically proved unpromising. Photolysis of solutions of iodoester (1a) at 254 nm generated mixtures which contained no significant amounts of unsaturated lactones. The major reaction product isolated was the unsaturated ester (2). Ester (2) was synthesised independently by esterification of propynoic acid with 2-cyclohexen-1-ol.



(1)

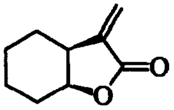


(2)

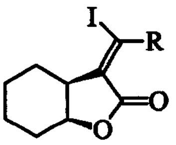
Used throughout :

(a) R = H; (b) $R = CH_3$;
(c) $R = CH_3CH_2$ (d) $R = (CH_3)_2CH$
(e) $R = (CH_3)_3C$ (f) $R = Si(CH_3)_3$

Zinc metal has been used to reduce side reactions and to increase yields in photolyses of alkyl halides. The success of this has been attributed to the removal of HI and/or I_2[7,8]. In subsequent photolyses of the iodo acetylenic esters a fine grade of zinc powder was suspended in the photolysis vessel by a stream of nitrogen gas. Reaction of (1a) in this manner gave mixtures containing unchanged (1a), small quantities of both the unsaturated ester (2) and the methylene lactone (3), and the iodomethylene lactones (4a) and (5a). The fact that the product mixtures showed some variability in composition from run to run was probably a reflection of the inhomogeneity of the reaction medium. When photolysis was stopped at the stage when approximately 70% of the reactant had been consumed, the combined yield of (4a) and (5a) was 30-40%.



(3)



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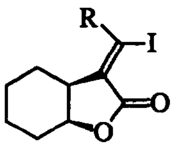


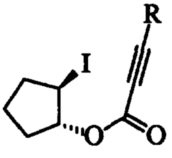
(5)

The (*E*)-isomer dominated over the (*Z*), generally to the extent of >2:1. Longer photolysis times produced a significant drop in the overall yield of the lactone products as well as a decrease in the (*E*) to (*Z*) ratio. Photolyses of other iodo acetylenic esters in the presence of zinc also gave rise to iodoalkylidene lactones (Table 1). Yields were improved when the triple bond bore a methyl group and again both (*E*) and (*Z*)-geometric isomers were formed. No alkylidene lactone formation was observed in these cases.

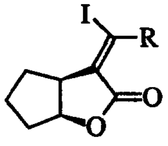
Table 1. Iodo Acetylenic Ester Photocyclisations

Ester	Time (h)	Solvent/ metal	Reactant	Products (Isolated % yield) (E)-iodo lactone	(Z)-iodo lactone	Alkylidene lactone	Alkene
(1a)	4.3	Bu^{t}OH/none	-	-	-	-	(2) 79%
(1a)	0.7	CH_3CN/Zn	(1a) 39%[†]	(4a) 15%	(5a) 7%[†]	(3a) 2%[†]	(2) 2%[†]
(1a)	2.0	Bu^{t}OH/Mg	(1a) 52%[†]	(4a) 31%[†]	(5a) 14%[†]	(3a) <1%[†]	-
(1b)	0.4	CH_3CN/Zn	(1b) 37%	(4b) 47%	(5b) 11%	-	-
(6a)	0.1	CH_3CN/Zn	(6a) 64%	(7a) 21%	(8a) 3%	(9a) <1%	-
(6b)	0.3	CH_3CN/Zn	(6b) 36%	(7b) 25%	(8b) 29%	-	-

[†] Estimated from ^{1}H NMR spectra of mixtures.



(6)



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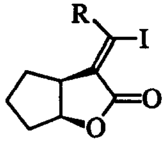
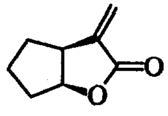


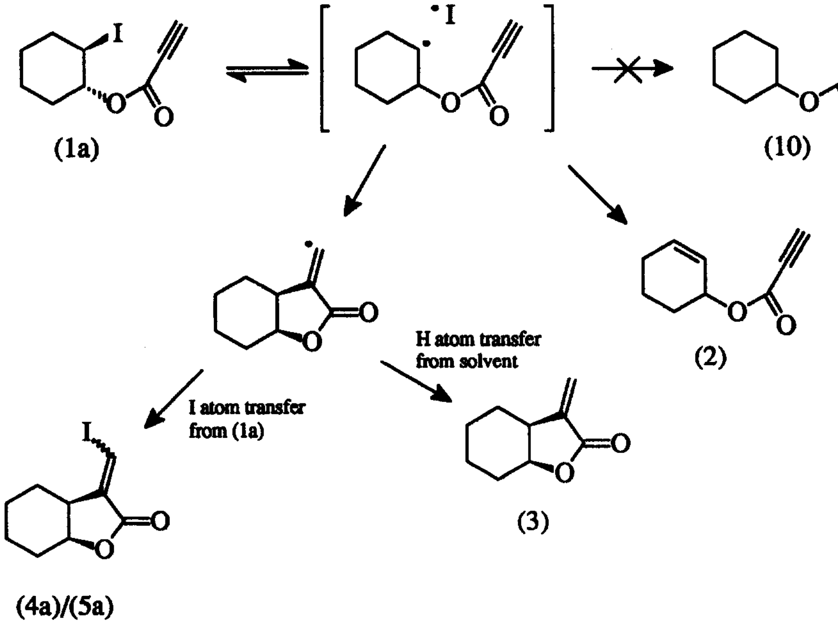
(8)



(9)

The intermediates in this photocyclisation probably have excess energy and would thus be prone to loss of stereochemical integrity. Photoisomerisation of the products could also result in lack of stereospecificity, consistent with the observation that longer photolysis times resulted in an increase in the proportion of the (*Z*)-isomer. As the iodoalkylidene lactones have much higher molar absorptivity than the iodoester substrates at similar absorption wavelengths (*c.a.* 7 times as high), the proportion of light absorbed by substrate molecules will fall off dramatically as the reaction proceeds. This may account for the relatively low yields and the low mass recoveries.

Once the n-σ^* transition has occurred in the photolysis of an iodo acetylenic ester such as (1a), several possible fates await the ensuing radical pair (Scheme 3). Recombination will return (1a). Radical cyclisation leads to the iodinated lactones (4a) and (5a) if an iodine-atom transfer takes place, or to the methylene lactone (3) following a hydrogen-atom transfer from the solvent. Hydrogen atom transfer is apparently slow relative to the *exo dig* cyclisation process and no cyclohexyl propynoate (10) was detected.



Scheme 3

Elimination to form the unsaturated ester (2) could take place by carbenic or carbocationic pathways, both of which require the involvement of the iodine atom in the radical pair (Scheme 2). One possible role for the zinc is to remove the iodine radical from competition and allow the carbon free radical to cyclise preferentially. Zinc may bind to the alkyl halide before photolytic cleavage, or may trap the iodine atom after radical pair formation. Alternatively, zinc may recycle carbocations by transfer of an electron to regenerate the carbon free radical. In addition, the production of significant quantities of (4a) and (5a) requires an efficient iodine atom transfer cycle. If the vinyl radical reacts with molecular iodine this process will be disrupted. Zinc may play a part in preventing this sequence also. It was also noted that production of (4a) and (5a) did not result merely from reaction of the alkyl halide with the metal, but required photolytic initiation. Magnesium also effected the same results.

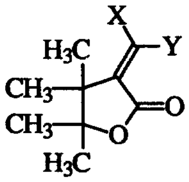
ISOMERISATION OF IODOALKYLIDENE LACTONES

Dibenzoyl peroxide cyclisation of iodo acetylenic esters had provided good yields of (*E*)-iodoalkylidene lactones in most cases[1]. However, while photolytic cyclisation had given significant proportions of the (*Z*)-isomers, overall yields and recoveries were poor. The fact that the proportion of the (*Z*)-isomer in the photolysis mixture increased with time suggested that photoisomerisation of the (*E*)-iodoalkylidene lactones might provide a convenient route to the (*Z*)-species.

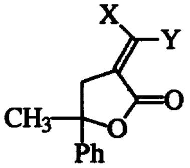
Brief photolysis of the (*E*)-iodomethylene lactone (7b) at 235 nm in acetonitrile in the presence of zinc gave a product with an (*E*) to (*Z*) ratio of 11:1. Under these conditions, little of the ethylidene lactone was produced. Photolysis in the absence of zinc gave a better result with equal amounts of the (*E*) and (*Z*)-iodoethylidene lactones being formed. Similar photolyses conducted on other (*E*)-iodoalkylidene lactones gave mixtures of (*E*) and (*Z*)-isomers from which pure samples of the (*Z*) isomers could be isolated (Table 2). A 1:1 ratio of isomers was achieved for most derivatives. Formation of the alkylidene lactones could be minimised by keeping the photolysis time short (15-30 min). This was less of a problem when the double bond had an alkyl substituent.

Table 2. Photoisomerisations of (*E*)-Iodoalkylidene Lactones

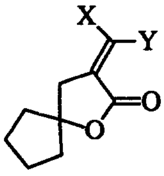
(*E*)-Lactone reactant	Time (min)	Isolated yield (*E*)+(*Z*) (%)	(*Z*)-Lactone product	% (*Z*)-Lactone in lactone mixture
(4a)	30	70	(5a)	50
(4b)	15	90	(5b)	50
(4f)	30	73	(5f)	50
(7a)	60	88	(8a)	42
(7b)	30	60	(8b)	50
(7c)	40	53	(8c)	34
(7d)	40	53	(8d)	30
(7e)	30	56	(8e)	61
(7f)	30	61	(8f)	49
(11b)	30	77	(12b)	34
(13)	60	53	(14)	45
(15)	15	71	(16)	38
(17)	15	52	(18)	54



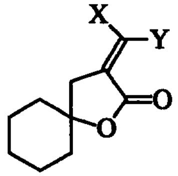
(11) X = I; Y = R
(12) X = R; Y = I



(13) X = I; Y = H
(14) X = H; Y = I



(15) X = I; Y = H
(16) X = H; Y = I



(17) X = I; Y = H
(18) X = H; Y = I

DOUBLE-BOND STEREOCHEMISTRY

^1H NMR data for pairs of (*E*) and (*Z*)-iodoalkylidene lactones are given in Table 3. Stereochemical assignments for several of the iodomethylene and iodoethylidene pairs were verified by nuclear Overhauser enhancement experiments. For example, irradiation of the vinylic proton signal of the iodomethylene derivative (5a) which has the (*Z*)-stereochemistry about the double bond, resulted in an enhancement of ring proton signals. A similar experiment on the (*E*)-isomer produced none. In the ^1H NMR spectra of conjugated *exo*-methylene ketones, the resonance of the vinylic proton located *cis* to the carbonyl group exhibits significant deshielding (0.6-0.9 ppm) compared to that of the *trans* proton[9,10]. Corresponding variations have been used to distinguish between the geometric isomers of β-substituted-α-methylene lactones in previous studies (*e.g.* ref. 11). Data for the iodomethylene lactones produced in this work show similar trends (Table 3), as the (*E*)-iodomethylene derivatives have vinylic proton resonances deshielded by 0.4-0.7 ppm relative to their (*Z*)-counterparts. Allylic proton signals are similarly deshielded (0.2-0.6 ppm). Protons further removed from the double bond are affected less and are in some cases slightly more shielded in the (*E*)-isomer.

^{13}C NMR spectral data for the carbonyl carbon and the alkenyl carbons are presented in Table 4. The carbonyl carbon resonance for the (*E*)-derivatives appeared between δ 163.4 and 167.6 while the corresponding values for the (*Z*)-isomers ranged from δ 167.4 to 169.8. For each isomeric pair, the carbonyl carbon signal for the (*E*)-isomer was the more shielded; this effect increased with bulk of the alkyl substituent. Similar trends were apparent for the doubly-bonded carbons, although these chemical shift differences were masked somewhat by the substituent effects of the groups on the exocyclic carbon. The β-carbon signal of the (*E*)-

isomer was significantly downfield of that for the (Z)-form (Δδ 5.5-11.5 ppm), and, with one exception [compounds (11a)/(12a)] the α-carbon was similarly deshielded. These trends in the ^{13}C NMR data could also be of use in assigning the stereochemistry.

Table 3. ^{1}H NMR Data for Alkylidene Grouping of (*E*) and (*Z*)-Iodoalkylidene Lactones

	(*E*)-Isomers[1]				(*Z*)-Isomers		
Cpd	Vinylic proton	Allylic protons	Other protons	Cpd	Vinylic proton	Allylic protons	Other protons
(4a)	7.59,d,***2***†	-	-	(5a)	7.11,d,***3***†	-	-
(4b)	-	3.05,d,***1***†	-	(5b)	-	2.75,s†	-
(4f)	-	-	0.08,s	(5f)	-	-	0.36,s
(6a)	7.79,d,***2***†	-	-	(7a)	7.32,d,***2***†	-	-
(6b)	-	3.12,d,***2***†	-	(7b)	-	2.80,d,***1***†	-
(6c)	-	3.34,dq,***2***,***7***	1.12,t,***7***	(7c)	-	2.80,q,***7***	1.19,t,***7***
(6d)	-	3.96,sept,***6***	0.97,d,***6***;0.98,d,***6***	(7d)	-	2.47,sept,***7***	1.05,d,***7***;1.09,d,***7***
(6e)	-	-	1.47,s	(7e)	-	-	1.45,s
(6f)	-	-	0.34,s	(7f)	-	-	0.38,s
(11a)	7.72,s	-	-	(12a)[1]	7.04,s	-	-
(11b)	-	3.25,s†	-	(12b)	-	2.94,s†	-
(13)	7.86,dd,***3***,***3***	-	-	(14)	7.35,dd,***3***,***3***	-	-
(15)	7.77,dd,***3***,***3***	-	-	(16)	7.20,dd,***3***,***3***	-	-
(17)	7.79,dd,***3***,***3***	-	-	(18)	7.20,dd,***3***,***3***	-	-

Irradiation of signals labelled † produced no n.O.e enhancements for the (*E*)-isomers but gave enhancements of ring proton signals for the (*Z*)-isomers. Values for all resonances are in ppm downfield from $(CH_3)_4Si$ and coupling constants (Hz) are shown in ***bold italic***.

Table 4. Selected ^{13}C NMR Data for (*E*) and (*Z*)-Iodoalkylidene Lactones

	(*E*)-Isomers[1]				(*Z*)-Isomers		
Cpd	Alkenyl carbons β	α	Carbonyl carbon	Cpd	Alkenyl carbons β	α	Carbonyl carbon
(4a)	90.7	146.4	166.7	(5a)	83.8	140.1	168.5
(4b)	115.1	139.5	165.2	(5b)	103.3	137.0	168.7
(4f)	127.0	152.9	165.0	(5f)	116.3	147.1	168.2
(6a)	94.8	144.2	166.7	(7a)	87.5	140.1	168.3
(6b)	120.1	136.9	165.2	(7b)	106.1	134.3	168.4
(6c)	131.7	136.2	164.9	(7c)	117.5	133.4	168.5
(6d)	134.4	144.2	165.0	(7d)	129.2	132.0	168.6
(6e)	138.1	144.6	163.4	(7e)	131.4	133.0	169.8
(6f)	131.9	151.0	165.1	(7f)	120.4	144.4	167.9
(11a)	90.4	145.5	167.6	(12a)[1]	83.3	146.3	167.7
(13)	94.5	144.4	165.0	(14)	86.1	144.0	167.4
(15)	93.3	141.2	165.3	(16)	84.8	135.9	167.6
(17)	94.0	140.9	165.2	(18)	85.2	135.5	167.6

Values are in ppm downfield from $(CH_3)_4Si$.

The UV data listed in Table 5 again shows a clear distinction between the (*E*) and (*Z*)-geometric isomers. The (*E*)-derivatives exhibit a lower wavelength of absorption (λ_{max}) than their (*Z*)-counterparts. With the exception of the *tert*-butyl and trimethylsilyl derivatives, the maxima for the (*E*)-compounds fall in a narrow range of 246-254 nm while the (*Z*)-compounds show an even smaller range of values (261-265 nm). The *tert*-

butyl and trimethylsilyl substituted lactones absorb at longer wavelength for both (*E*) and (*Z*)-geometries. IR data for the iodolactones are also presented in Table 5. For each isomeric pair the (Z)-form has the carbonyl band at the higher frequency. However, taken overall, the frequency ranges for the two geometries overlap considerably.

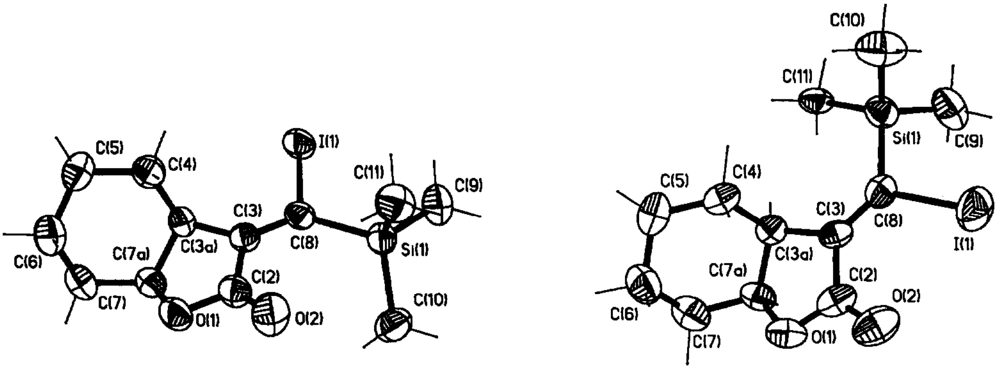
Table 5. Selected UV and IR Data for (*E*) and (*Z*)-Iodoalkylidene Lactones

	(*E*)-Isomers[1]			(*Z*)-Isomers	
Cpd	UV $\lambda_{max}(\varepsilon)$	IR $\nu_{C=O}$	Cpd	UV $\lambda_{max}(\varepsilon)$	IR $\nu_{C=O}$
(4a)	252 (6580)	1763	(5a)	261 (5100)	1776
(4b)	253 (6580)	1759	(5b)	261 (6120)	1771
(4f)	265 (8590)	1761	(5f)	274 (5240)	1767
(6a)	252 (8040)	1766	(7a)	265 (7500)	1774
(6b)	254 (11300)	1750	(7b)	262 (7930)	1759
(6c)	254 (8310)	1740[†]	(7c)	262 (8180)	1744[†]
(6d)	255 (8780)	1740[†]	(7d)	263 (5030)	1748[†]
(6e)	264 (6260)	1744[†]	(7e)	266 (5550)	1748[†]
(6f)	266 (4030)	1763	(7f)	277 (4860)	1768
(11a)	250 (9330)	1748[†]	(12a)[1]	261 (7260)	1754[†]
(11b)	253 (7080)	1753	(12b)	261 (3960)	1767
(15)	246 (11530)	1747[†]	(16)	262 (6360)	1754[†]
(17)	248 (9000)	1751[†]	(18)	261 (7940)	1753[†]

UV spectra were obtained as CH_3OH solutions. IR spectra were recorded as CCl_4 or $CHCl_3$ (†) solutions.

CRYSTAL STRUCTURES OF A PAIR OF IODOALKYLIDENE LACTONES

The trimethylsilyl substituted iodoalkylidene lactones (4f), (5f), (6f), and (7f) contain an interesting juxtaposition of functionality which potentially provides both carbanion and carbocation equivalencies at the same carbon atom. We are currently exploring ways of developing this potential. As both (4f) and (5f) were crystalline, it seemed appropriate to examine the solid state structures of this isomeric pair.



(4f) (5f)

Figure 1. ORTEP diagrams for TMS-substitututed iodoalkylidene lactones (4f) and (5f)

ORTEP diagrams for (4f) and (5f) are shown in Fig. 1. Bond lengths and bond angles are summarised in Table 6. In both compounds the cyclohexane ring is a flattened chair which is slightly skewed. These deviations from true chair conformations may result partly from the *cis* fusion and partly from crystal packing forces. In both structures the hydrogen attached to C3a experiences short intermolecular contacts (< 2.6 Å) with the ring oxygen in (4f) and the carbonyl oxygen in (5f). The five-membered rings in both structures adopt distorted β-envelope conformations. In (4f) the mean deviation for the C7a, O1, C2, C3 plane is 0.032 Å and for (5f) it is 0.036 Å; C3a is 0.53 Å and 0.51 Å above the plane, respectively. The C=C and C=O groups in both compounds do not lie in this plane. Both groups bend towards the cyclohexane ring and distortions from planarity are of similar magnitudes in both compounds. It is noteworthy that the C=C and C=O groups do not lie in a plane for either compound. In (4f) O2 is 0.27 Å above the C2, C3, C8 plane and Si1 is in the plane, while in (5f) O2 is 0.21 Å above and I1 0.05 Å below this plane. This corresponds to the conjugated C=C and C=O being out of planarity by 17.2° in (4f) and by 13.1° in (5f). The distance between O2 and the *cis* substituent in both compounds is similar [O2...C11 3.00 Å; O2...I1 3.13 Å]. The nature of these deviations suggests that the *cis* arrangement of trimethylsilyl or iodine has a similar steric impact on the carbonyl grouping in these compounds. Most importantly, the X-ray structural analyses bear out the stereochemical assignments which have been made earlier; the ring junction is *cis*, and the double bond stereochemistries have been correctly assigned.

Table 6. Bond lengths (Å) and angles (°) for (4f) and (5f)

Bond lengths (Å)				Bond angles (°)				
		(4f)	(5f)				(4f)	(5f)
I(1)	C(8)	2.119(3)	2.142(5)	C(8)	-Si(1)	-C(9)	109.4(1)	109.0(3)
Si(1)	C(8)	1.913(3)	1.895(6)	C(8)	-Si(1)	-C(10)	111.3(1)	105.3(3)
Si(1)	C(9)	1.861(3)	1.869(6)	C(8)	-Si(1)	-C(11)	106.1(1)	113.7(3)
Si(1)	C(10)	1.867(3)	1.850(6)	C(9)	-Si(1)	-C(10)	107.6(1)	112.6(4)
Si(1)	C(11)	1.855(3)	1.869(5)	C(9)	-Si(1)	-C(11)	109.1(1)	107.1(3)
O(1)	C(7a)	1.472(4)	1.465(6)	C(10)	-Si(1)	-C(11)	113.3(1)	109.3(3)
C(2)	C(3)	1.504(4)	1.509(8)	C(3)	-C(2)	-O(1)	108.5(2)	110.2(5)
C(2)	O(1)	1.354(4)	1.344(7)	C(3)	-C(2)	-O(2)	129.9(3)	128.7(7)
C(2)	O(2)	1.190(4)	1.203(6)	O(1)	-C(2)	-O(2)	121.6(3)	121.1(6)
C(3)	C(3a)	1.496(4)	1.515(7)	C(2)	-C(3)	-C(3a)	104.8(2)	103.1(5)
C(3)	C(8)	1.332(4)	1.314(7)	C(2)	-C(3)	-C(8)	122.3(3)	129.4(5)
C(4)	C(3a)	1.536(4)	1.557(6)	C(8)	-C(3)	-C(3a)	132.9(3)	127.5(5)
C(4)	C(5)	1.517(4)	1.520(7)	C(4)	-C(3a)	-C(3)	110.9(2)	109.1(4)
C(5)	C(6)	1.519(5)	1.502(8)	C(7a)	-C(3a)	-C(3)	101.2(2)	102.0(4)
C(6)	C(7)	1.504(5)	1.531(8)	C(7a)	-C(3a)	-C(4)	112.5(2)	112.8(4)
C(7)	C(7a)	1.516(4)	1.524(7)	C(5)	-C(4)	-C(3a)	112.7(2)	112.0(5)
C(7a)	C(3a)	1.522(4)	1.515(8)	C(4)	-C(5)	-C(6)	109.7(3)	110.7(5)
				C(5)	-C(6)	-C(7)	109.8(3)	111.0(5)
				C(6)	-C(7)	-C(7a)	113.3(3)	113.4(6)
				C(7)	-C(7a)	-C(3a)	117.0(3)	117.1(5)
				O(1)	-C(7a)	-C(3a)	103.4(2)	103.9(5)
				O(1)	-C(7a)	-C(7)	110.0(2)	109.7(5)
				I(1)	-C(8)	-Si(1)	114.6(1)	109.3(3)
				I(1)	-C(8)	-C(3)	115.7(2)	119.2(4)
				Si(1)	-C(8)	-C(3)	129.6(2)	131.4(4)
				C(2)	-O(1)	-C(7a)	109.6(2)	109.1(5)

CONCLUSIONS

Photoisomerisation of (*E*)-iodoalkylidene lactones gives mixtures of (*E*)- and (*Z*)-isomers which may be separated by chromatography to provide access to the (*Z*)-iodoalkylidene lactones. If short reaction times are used, conversion to iodine-free species is insignificant and the total recovery of iodinated lactones is excellent. Although a chromatographic separation is required, this is currently the only available general route to the (*Z*)-isomers. Use of the iodoalkylidene lactones in both isomeric forms has already been demonstrated in their reaction with lithium dimethylcuprate, where the iodine is replaced to give the alkylidene lactones with predominant retention of configuration[12]. Stereospecific replacement has been achieved in an analogous trifluoromethylation reaction[13] and work currently in progress shows similar behaviour with various nucleophilic reagents.

In most cases (*E*) and (*Z*)-iodoalkylidene lactones may be readily distinguished by their ^{1}H NMR spectra, but the ^{13}C NMR, IR and UV data which have been collated in this work should also provide useful parameters to aid in their stereochemical assignment.

EXPERIMENTAL

General

IR spectra were recorded on Perkin Elmer 1600 series or Nicolet 5MX Fourier transform spectrophotometers. High resolution spectra were run on a Digilab FTS-60 Fourier transform spectrophotometer in CCl_4. Frequencies (ν_{max}) are reported as cm^{-1}. Low resolution MS were recorded using a Varian MAT CH-7 mass spectrometer. High resolution MS were recorded by Dr P. Holland, Ruakura Research Centre, Private Bag Hamilton, N.Z. and by Dr H. Young, Fruit and Trees Division, DSIR, Auckland, N.Z. UV spectra were recorded on a Shimadzu UV 240 UV-visible spectrometer as methanol solutions. Wavelengths (λ_{max}) are reported as nm. Preparative layer chromatography (PLC) was performed on glass plates (20 cm x 20 cm) coated with a 1.25 mm layer of Merck silica gel $PF_{254+366}$. Radial chromatography was performed using a 'Chromatotron' model 7924 (Harrison Research, Palo Alto, U.S.A.) preparative centrifugal thin layer chromatograph. 1 mm, 2 mm and 4 mm silica gel layers were prepared and used according to the manufacturer's instructions. Unless otherwise stated, NMR spectra were obtained on a Varian VXR 300 instrument operating at 300 MHz for ^{1}H and at 75 MHz for ^{13}C. Some spectra were recorded on a Varian Gemini instrument operating at 200 MHz and 50 MHz for ^{1}H and ^{13}C respectively. Spectra were recorded as dilute $CDCl_3$ solutions and chemical shifts are quoted in ppm downfield from tetramethylsilane. Carbon types were determined either by DEPT or APT pulse sequences. Microanalyses were performed by Dr R.G. Cunninghame and associates of our Department.

Photolyses

Photolytic reactions were carried out in a Rayonet photochemical reactor at 254 nm using quartz vessels fitted with a nitrogen inlet. In all irradiations, the solutions were degassed by passage of nitrogen gas for 5 min. For irradiations conducted in the presence of metal powders, a steady stream of nitrogen was passed through the solution and the mixture was stirred with a teflon-coated magnetic stirrer bar.

Zinc dust was prepared by washing commercial zinc powder with dilute HCl (3 x 5%) using vigorous stirring, with a contact time of 2 min for each wash. Suction filtration of the clean zinc metal was followed by successive washes with water, acetone and ether. The metal was air dried and then suspended in the solvent which was to be used for the photolysis. Vigorous stirring was maintained for two min. after which time a one min. settling period was allowed before the supernatant liquid containing the finer grade of zinc metal was collected by decantation. Evaporation of the solvent gave the desired grade of metal powder.

Reactants

Iodo acetylenic esters and (*E*)-iodoalkylidene lactones were prepared according to reference 1.

Photocyclisations of Iodo Acetylenic Esters

A solution of the iodo acetylenic ester and the specified metal powder in the specified solvent was irradiated at 254 nm at room temperature. The mixture was stirred and was kept in a state of agitation by a constant stream of nitrogen gas. After the specified time, the reaction mixture was filtered, the solvent evaporated and the residue was filtered through alumina (CH_2Cl_2), followed by further purification as appropriate.

The following photolyses are reported according to the convention : ester (mass, amount), metal (mass, amount), solvent (volume), reaction time, experimental data.

Photocyclisations of (1a). (a) (1a) (0.210 g, 0.76 mmol), no metal powder, *tert*-butyl alcohol (20 ml), 4.3 h. The reaction mixture was poured into water (15 ml) and the aqueous layer was extracted with CH_2Cl_2 (4 x 5 ml). The combined organic extracts were washed with 10% $Na_2S_2O_3$ (10 ml) and dried ($MgSO_4$). Evaporation of the solvent gave a yellow oil (0.169 g, 79%) whose ^{1}H NMR spectrum was identical to that of an authentic sample of the unsaturated ester (2) (see later).

(b) (1a) (0.400 g, 1.4 mmol), zinc (0.420 g, 6.42 mmol), *tert*-butyl alcohol (40 ml), 3 h. Radial chromatography (40% CH_2Cl_2/hexane) gave : (i) unchanged (1a) (0.137 g, 34%); (ii) a mixture of the (*E*)[1] and (*Z*)-iodomethylene lactones (4a) and (5a) (0.096 g); (iii) a mixture of the (*Z*)-iodomethylene lactone (5a) and the methylene lactone (3a)[14,15] (0.096 g). Radial chromatography of the (*E*)/(*Z*) lactone mixture (20% EtOAc/hexanes) followed by PLC (20% Et_2O/hexanes) gave a pure sample of *(3Z,3aα ,7aα)-hexahydro-3-iodomethylene-2(3H)-benzofuranone (5a)*; IR (film) : 3056, 1633 (C=CH), 1745, 1255 (lactone); UV : 261 (ε 5100); ^{1}H NMR : 3.09 (ddd, *J* 6, 6, 6 Hz, 1H), 4.46 (ddd, *J* 6, 6, 6 Hz), 7.11 (d, *J* 3 Hz, 1H); ^{13}C NMR : 20.2 (CH_2), 21.4 (CH_2), 26.7 (CH_2), 28.5 (CH_2), 44.5 (CH), 75.4 (CH), 83.8 (CH), 140.1 (C), 168.5 (C); MS, *m/z* : 278 (M^+); Anal. Found : C, 38.9; H, 4.1, I, 45.5; Calc. for $C_9H_{11}IO_2$: C, 38.9; H, 4.0; I, 45.6%.

(c) (1a) (0.482 g, 1.7 mmol), zinc (0.210 g, 3.2 mmol), acetonitrile (7.5 ml), 40 min. Radial chromatography (25% Et_2O/hexanes) gave : (i) a mixture (0.201 g) of (1a) and unsaturated ester (2) in the ratio 20:1 (^{1}H NMR); (ii) (*E*)-iodomethylene lactone (4a), (0.072 g, 15%); (iii) A mixture (0.037 g) of the (*Z*)-iodomethylene lactone (5a) and the methylene lactone (3a) in the ratio of 7:2 (^{1}H NMR).

(d) (1a) (0.210 g, 0.76 mmol), magnesium (0.198 g, 8.1 mmol), *tert*-butyl alcohol (20 ml), 2 h. Flash chromatography gave a mixture (0.154 g) which contained (1a), methylene lactone (3a), and iodomethylene lactones (4a) and (5a) in the ratio 3.7:trace:2.3:1 (^{1}H NMR).

Photocyclisation of (1b). (1b) (0.440 g, 1.5 mmol), zinc (0.210 g, 3.2 mmol), acetonitrile (8 ml), 25 min. Radial chromatography (25% Et_2O/hexanes) gave : (i) unchanged (1b) (0.162 g, 37%); (ii) (*E*)-iodoethylidene lactone (4b)[1] (0.206 g, 47%); (iii) *(3Z,3aα ,7aα)-hexahydro-3-(1-iodoethylidene)-2(3H)-benzofuranone* (5b), (0.048 g, 11%), IR (film) : 1770, 1209 (lactone), 1640 (C=C); UV : 261 (ε 6120). ^{1}H NMR : 2.28 (m, $W_{h/2}$ 15 Hz, 1H), 2.75 (s, 3H), 3.16 (ddd, *J* 11, 7, 5 Hz, 1H), 4.35 (m, $W_{h/2}$ 11 Hz, 1H); ^{13}C NMR : 19.2 (CH_2), 22.9 (CH_2), 26.6 (CH_2), 26.9 (CH_2), 33.6 (CH_3), 42.1 (CH), 74.1 (CH), 103.3 (C), 137.0 (C), 168.7 (C); MS, *m/z* : 292 (M^+); Anal. Found : C, 41.0; H, 4.5; I, 43.5, Calc. for $C_{10}H_{13}IO_2$: C, 41.1; H, 4.5; I, 43.4%.

Photocyclisation of (6a). (6a) (0.315 g, 1.2 mmol), zinc (0.196 g, 3.0 mmol), acetonitrile (7 ml), 5 min. Radial chromatography (25% Et_2O/hexanes) gave : (i) unchanged (6a) (0.201 g, 64%); (ii) (*E*)-iodomethylene lactone (7a)[1] (0.066 g, 21%); (iii) A mixture (0.014 g) of the (*Z*)-iodomethylene lactone (8a) (see later) and the methylene lactone (9)[14,16] in the ratio of 28:1 (^{1}H NMR).

Photocyclisation of (6b). (6b) (0.250 g, 0.9 mmol), zinc (0.200 g, 3.1 mmol), acetonitrile (8 ml), 20 min. PLC (25% Et_2O/hexanes) gave : (i) unchanged (6b) (0.89 g, 36%); (ii) (*E*)-iodoethylidene lactone (7b)[1] (0.062 g, 25%); (iii) *(3Z,3aα ,6aα)-hexahydro-3-(1-iodoethylidene)-2H-cyclopenta[b]furan-2-one (8b)* (0.072 g, 29%); mp 59-60°; IR (film) : 1743, 1270, 1220 (lactone), 1630 (C=CH); UV : 262 (ε 7930); ^{1}H NMR : 2.80 (d, *J* 1 Hz, 3H), 3.58 (m, $W_{h/2}$ 16 Hz, 1H), 4.83 (m, $W_{h/2}$ 10 Hz, 1H); ^{13}C NMR : 23.2 (CH_2), 33.3 (CH_2), 33.7 (CH_2), 34.5 (CH_3), 45.6 (CH), 80.6 (CH), 106.1 (C), 134.3 (C), 168.4 (C); MS, *m/z* : 278 (M^+); Anal. Found : C, 38.8; H, 4.0; Calc. for $C_9H_{11}IO_2$: C, 38.9; H, 4.0%.

2-Cyclohexenyl propynoate (2)

A solution of 2-cyclohexen-1-ol (0.310 g, 3.2 mmol), propynoic acid (0.220 g, 3.1 mmol) and a small crystal of p-toluenesulfonic acid monohydrate in C_6H_6 (20 ml) was heated under reflux with a Dean-Stark trap. After 12.5 h the solvent was removed and the residue was taken up in ether (20 ml) and washed with saturated $NaHCO_3$ (2 x 15 ml). The organic layer was dried ($MgSO_4$) and the solvent removed to give a yellow oil which on radial chromatography (25% ethyl acetate/hexane) gave 2-cyclohexenyl propynoate (2) (0.037 g, 8%); IR (film) : 3280, 2120 (C≡CH), 3036, (C=CH), 1713, 1238 (ester); ^1H NMR : 2.87 (s, 1H), 5.36 (m, $W_{h/2}$ 10 Hz, 1H), 5,73 (m, $W_{h/2}$ 14 Hz, 1H), 6.02 (m, $W_{h/2}$ 16 Hz, 1H); ^{13}C NMR : 18.7 (CH_2), 24.9 (CH_2), 28.1 (CH_2), 70.5 (CH), 74.4 (CH), 75.1 (C), 124.3 (CH), 133.8 (CH), 152.4 (C); MS, *m/z* : 150(M^+); Anal. Found : C, 72.1, H, 6.5; Calc. for $C_9H_{10}O_2$: C, 72.0; H, 6.7%.

Photoisomerisations of (E)-Iodoalkylidene Lactones

A solution of the (*E*)-iodovinylidene lactone in acetonitrile was irradiated at 254 nm at room temperature for the specified time. Evaporation of the solvent was followed by flash chromatography on alumina (CH_2Cl_2).

The isomerisations of the following (*E*)-iodovinylidene lactones are reported according to the convention : lactone (mass, amount), volume of acetonitrile, reaction time, experimental data.

Photoisomerisation of (4a). (4a) (0.047 g, 0.17 mmol), 8.5 ml, 30 min. Flash chromatography gave a 1:1 mixture of the (*E*) and (*Z*)-lactones (4a) and (5a) (0.033 g, 70%) (^1H NMR).

Photoisomerisation of (4b). (4b) (0.084 g, 0.29 mmol), 8.5 ml, 15 min. Flash chromatography gave a 1:1 mixture of the (*E*) and (*Z*)-lactones (4b) and (5b) (0.076 g, 90%) (^1H NMR).

Photoisomerisation of (4f). (4f) (0.090 g, 0.26 mmol), 8.5 ml, 30 min. Flash chromatography gave a 1:1 mixture of (4f) and (5f) (0.066 g) (^1H NMR) which on PLC (25% Et_2O/hexanes) gave : (i) unchanged (4f) (0.032 g, 36%); (ii) *(3Z,3aα ,7aα)-hexahydro-3-[iodo(trimethylsilyl)methylene]-2(3H)-benzofuranone* (5f) (0.033 g, 37%); IR (film) : 1759, 1190, 1110 (lactone), 1630 (C=C); UV : 274 (ε 5240). ^1H NMR : 0.36 (s, 9H), 2.28 (m, $W_{h/2}$ 21 Hz, 2H), 3.18 (ddd, *J* 11, 7, 5 Hz, 1H), 4.36 (m, $W_{h/2}$ 9 Hz, 1H); ^{13}C NMR : 0.9 (CH_3), 19.0 (CH_2), 23.1 (CH_2), 26.8 (CH_2), 27.9 (CH_2), 44.9 (CH), 74.1 (CH), 116.3 (C), 147.1 (C), 168.2 (C); MS, *m/z* 350.0200 (M^+); $C_{12}H_{19}IO_2Si$ requires 350.0199.

Photoisomerisation of (7a). (7a) (0.300 g, 1.1 mmol), 20 ml, 60 min. Flash chromatography gave a 1.3:1 mixture of (7a) and (8a) (GC, ^1H NMR) which on PLC (25% Et_2O/hexanes) gave (i) (*E*)-iodomethylene lactone (7a) (0.153 g, 51%); (ii) *(3Z,3aα ,6aα)-hexahydro-3-(iodomethylene)-2H-cyclopenta[b]furan-2-one* (8a) (0.110 g, 37%); IR (CCl_4) : 1765, 1220 (lactone), 1632 (C=C); UV : 265 (ε 8100); ^1H NMR : 3.47 (m, $W_{h/2}$ 16 Hz, 1H), 4.91 (ddd, *J* 6, 6, 1 Hz), 7.32 (d, *J* 2 Hz); ^{13}C NMR : 23.1 (CH_2), 33.6 (CH_2), 35.5 (CH_2), 47.6 (CH), 81.8 (CH), 87.5 (CH), 140.1 (C), 179.8 (C); Anal. Found : C, 36.3; H, 3.3; I, 47.9; Calc. for $C_8H_9IO_2$: C, 36.4; H, 3.4; I, 48.1%.

Photoisomerisations of (7b). (a) (7b) (0.047 g, 0.17 mmol), 7.5 ml, 30 min. Flash chromatography gave a 1:1 mixture of the (*E*) and (*Z*)-lactones (7b) and (8b) (0.028 g) (^1H NMR).

(b) (12b) (0.246 g, 0.88 mmol), 6 ml, 10.5 min, with zinc powder (0.100 g, 1.5 mmol). Flash chromatography gave an 11:1 mixture of (7b) and (8b) (0.230 g) (^1H NMR).

Photoisomerisation of (7c). (7c) (0.088 g, 0.30 mmol), 7.5 ml, 40 min. PLC (25% $CHCl_3$/C_6H_6) gave : (i) unchanged (7c) (0.031g, 35%); (ii) *(3Z,3aα ,6aα)-hexahydro-3-(1-iodopropylidene)-2H-cyclopenta[b]furan-2-one* (8c) (0.016 g, 18%); IR ($CHCl_3$) 1744 (C=O), 1619 (C=C); UV : 262 (ε 8180); ^1H NMR : 1.19 (t, *J* 7 Hz, 3H), 2.80 (q, *J* 7 Hz, 2H), 3.57 (m, $W_{h/2}$ 18 Hz, 1H), 4.81 (m, $W_{h/2}$ 9 Hz, 1H); ^{13}C NMR : 14.0 (CH_3), 23.3 (CH_2), 33.6 (CH_2), 33.9 (CH_2), 38.7 (CH_2), 45.6 (CH), 80.7 (CH), 117.5 (C), 133.4 (C); MS *m/z* 291.9916; Calc for $C_{10}H_{13}IO_2$ 291.9962.

Photoisomerisation of (7d). (7d) (0.126 g, 0.41 mmol), 8 ml, 40 min. PLC (30% $CHCl_3/C_6H_6$) gave : (i) unchanged (7d) (0.047 g, 37%); (ii) *(3Z,3aα ,6aα)-hexahydro-3-(1-iodomethylpropylidene)-2H-cyclopenta[b]furan-2-one* (8d) (0.020 g, 16%); IR ($CHCl_3$) 1748 (C=O), 1613 (C=C); UV : 263 (ε 5032); ^{1}H NMR : 1.05 (d, *J* 7 Hz, 3H), 1.09 (d, *J* 7 Hz, 3H), 2.47 (septet, *J* 7 Hz, 1H), 3.59 (m, $W_{1/2}$ 20 Hz, 1H), 4.82 (m, $W_{1/2}$ 14 Hz, 1H); ^{13}C NMR : 22.9 (CH_2), 23.3 (CH_3), 23.5 (CH_3), 33.7 (CH), 34.1 (CH_2), 38.4 (CH_2), 46.0 (CH), 81.0 (CH), 129.2 (C), 132.0 (C), 168.6 (C); MS *m/z* 306.0126; Calc for $C_{11}H_{15}IO_2$ 306.0119.

Photoisomerisation of (7e). (7e) (0.089 g, 0.28 mmol), 7.5 ml, 30 min. PLC (25% Et_2O/hexanes) gave : (i) unchanged (7e) (0.020 g, 22%); (ii) *(3Z,3aα ,6aα)-hexahydro-3-(1-iodo-2,2-dimethylpropylidene)-2H-cyclopenta[b]furan-2-one* (8e) (0.030 g, 34%); IR ($CHCl_3$) 1748 (C=O), 1580 (C=C); UV : 266 (ε 5549); ^{1}H NMR : 1.45 (s, 9H), 3.92 (m, $W_{1/2}$ 20 Hz, 1H), 4.67 (m, $W_{1/2}$ 12 Hz, 1H); ^{13}C NMR : 23.2 (CH_2), 32.4 (3 x q), 32.9 (CH_2), 34.9 (CH_2), 44.0 (C), 47.0 (CH), 80.5 (CH), 131.4 (C), 133.0 (C), 169.8 (C); MS *m/z* 320.0276. Calc for $C_{12}H_{17}IO_2$ 320.0275.

Photoisomerisation of (7f). (7f) (0.070 g, 0.21 mmol), 8.5 ml, 30 min. Flash chromatography gave a 1:1 mixture of (7f) and (8f) (0.060 g) which on PLC (25% Et_2O/hexanes) gave : (i) unchanged (7f) (0.022 g, 31%); (ii) *(3Z,3aα ,6aα)-hexahydro-3-[iodo(trimethylsilyl)methylene]-2H-cyclopenta[b]furan-2-one* (8f) (0.021 g, 30%); IR (film) : 1760, 1250 (lactone), 1610 (C=C); UV : 277 (ε 4860). ^{1}H NMR : 0.38 (s, 9H), 1.99 (m, $W_{1/2}$ 24 Hz), 2.19 (m, $W_{1/2}$ 17 Hz, 2H), 3.60 (ddd, *J* 8, 6, 2 Hz, 1H), 4.81 (dd, *J* 6, 4 Hz, 1H); ^{13}C NMR : 0.7 (CH_3), 23.1 (CH_2), 33.3 (CH_2), 36.1 (CH_2), 47.6 (CH), 80.9 (CH), 120.4 (C), 144.4 (C), 167.9 (C); MS, *m/z* 336.0045 (M^+); Calc. for $C_{11}H_{17}IO_2Si$: 336.0043.

Photoisomerisation of (11b). (11b) (0.078 g, 0.27 mmol), 8.5 ml, 30 min. Flash chromatography gave a 2.2:1 mixture of (11b) and (12b) (0.063 g) (^{1}H NMR) which on PLC (25% Et_2O/hexanes) gave : (i) unchanged (11b) (0.040 g, 51%); (ii) *(Z)--3-(1-iodoethylidene)-4,4,5,5-tetramethyldihydro-2(3H)-furanone* (12b) (0.020 g, 26%) ; IR (CCl_4) : 1767, 1231 (lactone), 1624 (C=C); UV : 261 (ε 3960). ^{1}H NMR : 1.17 (s, 3H); 1.26 (s, 3H); 1.29 (s, 3H), 1.35 (s, 3H), 2.94 (br. s, 3H); MS, *m/z* : 294 (M^+); Anal. Found : C, 40.9; H, 5.3; I, 43.0; Calc. for $C_{10}H_{15}IO_2$: C, 40.8; H, 5.1; I, 43.2%.

Photoisomerisation of (13). (13) (0.040 g, 0.13 mmol), 4 ml, 1 h. PLC (25% Et_2O/hexane) gave (i) unchanged (13) (0.010 g, 29%); (ii) *(3Z)-dihydro-3-iodomethylene-5-methyl-5-phenyl-2(3H)-furanone* (14) (0.010 g, 24%); IR (CCl_4) 1755 (C=O); ^{1}H NMR : 1.73 (s, 3H); 3.17 (d, *J* 2 Hz, 2H); 7.35 (t, *J* 2 Hz, 1H); 7.36 (s, 5H); ^{13}C NMR : 29.9 (CH_3); 46.9 (CH_2); 82.7 (C); 86.1 (CH); 124.2 (CH); 127.9 (CH); 128.8 (CH); 134.9 (C); 144.0 (C); 167.4 (C); MS : *m/z* 313.9804 (M^+); Calc. for $C_{12}H_{11}IO_2$: 314.9805.

Photoisomerisation of (15). (15) (0.080 g, 0.31 mmol), 8 ml, 15 min. PLC (25% Et_2O/hexane) gave (i) unchanged (15) (0.040 g, 44%); (ii) *(3Z)-3-iodomethylene-1-oxaspiro[4.5]nonan-2-one* (16) (0.021 g, 27%); IR (film) : 3052, 1642 (=C-H), 1754 (C=O); UV : 262 (ε 6363); ^{1}H NMR : 1.71 (m, $W_{1/2}$ 5 Hz, 4H); 1.88 (m, $W_{1/2}$ 19 Hz, 2H); 2.02 (m, $W_{1/2}$ 20 Hz, 2H); 2.94 (d, *J* 2 Hz, 2H); 7.20 (t, *J* 2 Hz, 1H); ^{13}C NMR : 23.6 (CH_2); 39.0 (CH_2); 42.7 (CH_2); 84.8 (CH); 90.6 (C); 135.9 (C); 167.6 (C); Anal. Found : C, 38.8; H, 4.1; I, 45.8; Calc. for $C_9H_{11}IO_2$: C, 38.9; H, 3.9; I, 45.6%.

Photoisomerisation of (17). (17) (0.790 g, 0.27 mmol), 6 ml, 15 min. PLC (25% Et_2O/hexane) gave (i) unchanged (17) (0.020 g, 24%); (ii) *(3Z)-3-iodomethylene-1-oxaspiro[4.5]decan-2-one* (18) (0.021 g, 28%); IR (film) : 3045 (=C-H), 1753 (C=O), 1624 (C=C); UV : 261 (ε 7940); ^{1}H NMR (200 MHz) : 1.51 (m, 4H); 1.77 (m, 4H); 2.74 (d, J 2 Hz, 2H); 7.20 (t, J 2 Hz, 2H); ^{13}C NMR (50 MHz) : 22.5 (CH_2); 24.7 (CH_2); 37.3 (CH_2); 43.9 (CH_2); 82.1 (C); 85.2 (CH); 135.5 (C); 167.6 (C); Anal. Found : C, 40.8; H, 4.3; Calc. for $C_{10}H_{13}IO_2$: C, 41.1; H, 4.4%.

X-ray Analysis of (4f) and (5f)

Crystal data. (4f): $C_{12}H_{19}IO_2Si$; $M = 350.26$; monoclinic, $P2_1/c$; a 6.283(2), b 20.775(3), c 11.033(1) Å; β 90.50 (1)°; V 1440.1(4) Å^3; D_c 1.62 g cm^{-3}; Z 4; $F(000)$ 696; λ 0.71069 Å; μ(Mo Kα) 0.23 cm^{-1}; T 298 K; crystal decay < 8%; crystal size 0.67 x 0.58 x 0.53 mm. (5f): $C_{12}H_{19}IO_2Si$; $M = 350.26$; monoclinic, $P2_1/c$; a 10.089(3), b 11.054(3), c 13.685(4) Å; β 101.70 (2)°; V 1496.6(7) Å^3; D_c 1.56 g cm^{-3}; Z 4; $F(000)$ 696; λ 0.71069 Å; μ(Mo Kα) 0.22 cm^{-1}; T 153 K; crystal decay < 3%; crystal size 0.50 x 0.43 x 0.12 mm.

Data Collection and Refinement. Preliminary photographic X-ray examination established the space group and approximate cell dimensions. An Enraf-Nonius CAD4 diffractometer was used in ω - 2θ mode to collect data for (4f) ($2\theta_{max}$ 50°) and a Nicolet P3 diffractometer was used for (5f) ($2\theta_{max}$ 52°). Final cell dimensions were obtained from 25 centred reflections (13 < 2θ < 34°). For (4f), 2523 reflections were collected and averaged to give 2264 unique reflections [$I > 2\sigma(I)$]; for (5f), 1982 reflections were collected and averaged to give 1597 unique reflections [$I > 2\sigma(I)$]. Lorentz and polarization corrections were applied[17] as was an empirical absorption correction for (4f) (transmission factors 0.99 - 0.93) and an analytical absorption correction for (5f) (transmission factors 0.77 - 0.38). The iodine atom in each structure was located from a Patterson synthesis, and all the other non-hydrogen atoms were found from difference syntheses. The structures were refined by full-matrix least squares with all non-hydrogen atoms anisotropic[18]. Hydrogen atoms were placed in idealized positions. Complex neutral atom scattering factors[19] were employed together with suitable weighting schemes. Refinements were continued until all calculated shifts were < 0.1σ; for (4f) $R = 0.0258$, $R_w = 0.0348$ for 142 variables and for (5f) $R = 0.0394$, $R_w = 0.0363$ for 154 variables. Final atomic coordinates are given in Table 7. Lists of structure factors, thermal parameters, hydrogen atom coordinates and other crystallographic data are available from the authors on request.

Table 7. Final positional parameters for (4f) and (5f)

		(4f)			(5f)	
	x/a	*y/b*	*z/c*	*x/a*	*y/b*	*z/c*
I(1)	0.1201(0)	0.3987(0)	-0.0037(0)	0.1839(1)	0.4229(0)	0.6380(0)
Si(1)	0.2273(1)	0.4512(0)	0.2818(1)	0.1481(2)	0.1726(1)	0.7608(1)
C(2)	-0.0707(5)	0.3223(2)	0.3520(3)	0.4904(8)	0.4227(5)	0.7956(4)
C(3)	-0.0255(4)	0.3360(1)	0.2208(2)	0.3953(6)	0.3196(4)	0.8043(4)
C(3a)	-0.1386(4)	0.2838(1)	0.1525(2)	0.4739(7)	0.2458(4)	0.8900(3)
C(4)	-0.3686(5)	0.3037(1)	0.1224(3)	0.4385(6)	0.2909(5)	0.9894(3)
C(5)	-0.5124(5)	0.2464(2)	0.0978(3)	0.5462(7)	0.2560(6)	1.0795(4)
C(6)	-0.5151(5)	0.2027(2)	0.2081(3)	0.6812(7)	0.3075(6)	1.0713(4)
C(7)	-0.2954(5)	0.1767(2)	0.2320(3)	0.7264(7)	0.2591(6)	0.9784(4)
C(7a)	-0.1274(5)	0.2287(2)	0.2433(3)	0.6190(7)	0.2725(5)	0.8831(4)
C(8)	0.0916(5)	0.3860(1)	0.1861(3)	0.2733(7)	0.2979(5)	0.7520(4)
C(9)	0.4197(6)	0.4962(2)	0.1865(4)	0.0853(8)	0.1080(6)	0.6336(4)
C(10)	0.3791(4)	0.4153(1)	0.4114(2)	0.0121(7)	0.2451(6)	0.8126(5)
C(11)	0.0129(4)	0.5067(1)	0.3302(2)	0.2220(6)	0.0448(4)	0.8436(4)
O(1)	-0.1457(4)	0.2614(1)	0.3611(2)	0.6149(5)	0.3982(3)	0.8487(3)
O(2)	-0.0554(4)	0.3565(1)	0.4381(2)	0.4668(5)	0.5160(4)	0.7503(3)

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