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Synthesis of Iodoalkylidene Lactones From Alkenes

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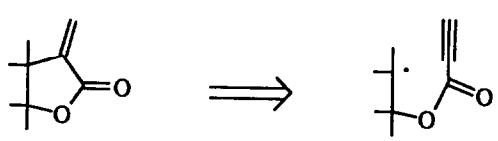
Abstract - *Alkenes are readily transformed into iodo acetylenic esters by addition of acetylenic acids in the presence of a source of iodonium ion. A subsequent free-radical cyclisation induced by dibenzoyl peroxide leads to (E)-iodoalkylidene butyrolactones.*

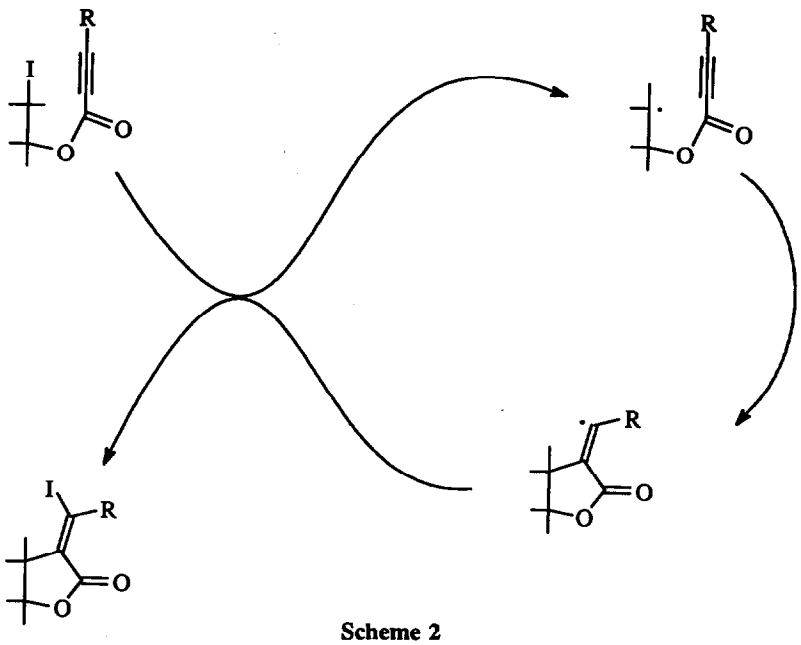
INTRODUCTION

α-Methylene butyrolactones have attracted considerable attention as a result of their considerable pharmacological activity. A review published in 1985[1] summarised retrosynthetic pathways available for the construction of this sub-unit. One key bond dissection which was relegated to the miscellaneous category was that shown in Scheme 1.



Scheme 1

The *exo-dig* ring closure required here is well known in free radical chemistry, and has been used for the creation of methylene cyclopentane derivatives and also, indirectly, for the creation of α-methylene butyrolactones. These latter syntheses have involved cyclisation of either propargyl ethers[2] or acetylenic acetals[3,4]. In both cases an oxidative process was required to complete the synthesis. We sought to achieve the same result more directly by employing acetylenic esters as our cyclisation substrates and have achieved this goal by means of the chain transfer reaction summarised in Scheme 2[5].

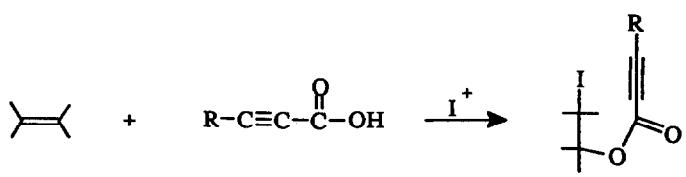


Scheme 2

The iodoalkylidene lactones represent an interesting combination of chemical functionality which has considerable potential for further modification. We have published details of replacement of the iodine by either the alkyl group of a lithium dialkylcuprate or by a hydrogen in a photochemical process[6]. This paper describes the formation of the iodoalkylidene lactones in more detail.

CYCLISATION PRECURSORS

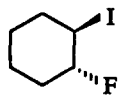
The retrosynthesis outlined in Scheme 1 requires a function capable of generating a free-radical. An alkyl iodide seemed appropriate as it has a suitably low bond dissociation energy and it could be readily introduced by electrophilic attack on an alkene. All the desired functionality could be added to a double bond in one step by using an acetylenic acid as the nucleophilic partner (Scheme 3).



Scheme 3

Two sources of iodonium ion proved satisfactory; bis(pyridine)iodine(I) tetrafluoroborate[7] and N-iodosuccinimide[8]. With $I(py)_2BF_4$, addition of stoichiometric amounts of either HBF_4 or $BF_3.Et_2O$ increased the yields by five to ten percent, possibly by removing the released pyridine, a potential competing

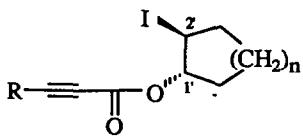
nucleophile[7]. High reactant concentrations proved essential as reaction with cyclohexene and propynoic acid at low concentration produced some 2-fluoroiodocyclohexane[7] (1). This compound could be prepared readily by reaction of cyclohexene with $I(py)_2BF_4$ in the absence of an additional nucleophile. Monitoring of the addition reaction by gas chromatography revealed that reaction times longer than those reported resulted in significant product degradation. N-iodosuccinimide gave more reproducible yields in larger scale reactions and proved preparatively simpler.



(1)

A selection of iodoesters was prepared according to Scheme 3. Results are summarised in Table 1. This approach has been used previously for the formation of simple esters and the reaction has been shown to yield products with a *trans* geometry[8]. In support of this, the H-1' and H-2' proton NMR signals for the cyclohexyl derivatives prepared in this work showed coupling constants consistent with a *trans* diequatorial orientation for the two attached groupings. While the corresponding signal multiplicities for the five, seven and eight-membered ring derivatives did not permit a definitive assignment of the stereochemistry, there is no reason to believe that they might be *cis*. In all cases only one geometric isomer was isolated.

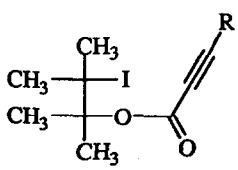
The regioselectivity of the reactions in the cases of indene and styrene is as expected on the basis of the stability of potential carbocation intermediates. The ^{13}C NMR spectrum of the styrene addition product (7a) had the methylene carbon resonance at δ 6.2 in accordance with a CH_2I grouping. Ultimate proof of the orientation of the addition to indene came after isolation of the product of its free-radical cyclisation (see later).



(2) n = 1
(3) n = 2
(4) n = 3
(5) n = 4

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 = $(CH_3)_3Si$
(g) R = C_6H_5



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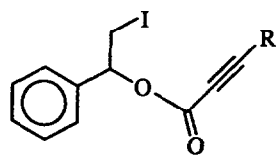

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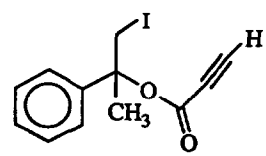
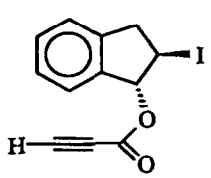


(8)

Table 1. Iodo Acetylenic Ester Preparations

Compound	Isolated Yield (%)		^{1}H NMR Signals[a]	
	Method A[b]	Method B[c]	CHI	CHOCOR
(2a)	78	80	4.27 ($W_{N/2}$ 15)	5.43 ($W_{N/2}$ 14)
(2b)	78	-	4.25 ($W_{N/2}$ 12)	5.39 ($W_{N/2}$ 11)
(2c)	72	-	4.26 ($W_{N/2}$ 11)	5.39 ($W_{N/2}$ 11)
(2d)	79	-	4.27 ($W_{N/2}$ 17)	5.39 ($W_{N/2}$ 9)
(2e)	63	-	4.27 ($W_{N/2}$ 11)	5.39 ($W_{N/2}$ 13)
(2f)	65	-	4.08 ($W_{N/2}$ 11)	5.22 ($W_{N/2}$ 11)
(2g)	94	-	4.31 ($W_{N/2}$ 12)	5.47 ($W_{N/2}$ 11)
(3a)	87	79	4.07 (*J* 11,9,4)	4.95 (*J* 9,9,5)
(3b)	86	-	4.09 (*J* 9,9,5)	4.99 (*J* 11,9,4)
(3f)	74	-	3.94 ($W_{N/2}$ 24)	4.82 ($W_{N/2}$ 22)
(3g)	73	-	4.15 (*J* 10,10,4)	5.08 (*J* 9,9,5)
(4a)	85	54	4.33 (*J* 8,8,4)	5.27 (*J* 8,8,3)
(4b)	93	-	4.28 (*J* 8,8,4)	5.19 (*J* 8,8,4)
(5a)	85	-	4.42 (*J* 10,6,3)	5.32 (*J* 10,7,3)
(5b)	90	-	4.42 (*J* 10,6,3)	5.29 (*J* 10,8,2)
(6a)	72		-	-
(6b)	60	-	-	-
(7a)	69	-	3.45(*J* 11,5);3.54 (*J* 11,8)	5.96 (*J* 8,6)
(7b)	99	-	3.46 (*J* 11,6);3.52 (*J* 11,8)	5.93 (*J* 8,6)
(8)	48	-	3.70 (*J* 11);3.79 (*J* 11)	-
(9)	83	-	3.81 (*J* 17,7)	4.57 (*J* 7,4,3)
(10)	52	-	3.79	-
(11)	33	-	3.74	-
(12)	11	-	3.70;3.90	-
(13)	29	-	3.70;3.94	-
(14)	78	-	4.58 ($W_{N/2}$ 16)	5.30 ($W_{N/2}$ 15)

[a] δ values for $CDCl_3$ solutions relative to $(CH_3)_4Si$. *J* and $W_{N/2}$ values in Hz.
[b] N-iodosuccinimide/acetylenic acid/alkene
[c] $I(py)_2BF_4$/acetylenic acid/alkene



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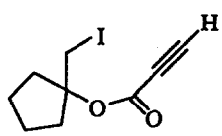

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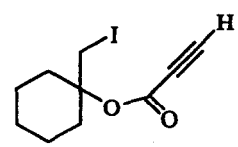

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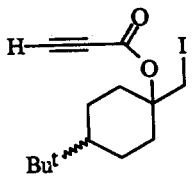

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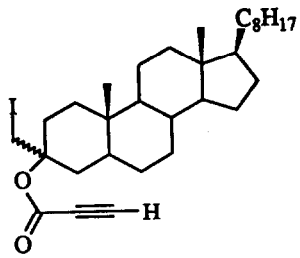

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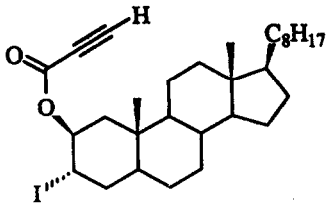
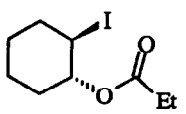


(14)

CHEMICALLY INDUCED CYCLISATION

Recent intense interest in free-radical chemistry has spawned many methods of radical induction. The procedures in vogue frequently involve tin species and use of these reagents has resulted in successful cyclisation of hexynyl iodides[9]. However, no alkylidene lactones were detected when (3a) was reacted with tributyltin hydride in the presence of azobisisobutyronitrile (AIBN). Starting material comprised the major portion of the recovered material, but a small portion of an uncharacterised tin containing species was also obtained. When the reaction was conducted in the presence of low concentrations of a tin reagent generated by the sodium borohydride reduction of tributyltin chloride[10], the sole reaction product was the saturated iodo propanoate (15). This substance was independently synthesised by reaction of cyclohexene with propanoic acid and N-iodosuccinimide. Reaction of (3a) with tributyltin hydride in the presence of an alternative free-radical initiator, dibenzoyl peroxide, gave a trace of the new compound, the iodomethylene lactone (19a). Reaction of the methyl substituted acetylene derivative (3b) with tributyltin hydride and AIBN gave a mixture of starting material and the iodoethylidene lactone (19b) in a ratio of 2:1. While these result showed promise, a superior method of cyclisation was ultimately developed and tin reagents were not further used. Attempted alkyl radical generation by electron transfer from a cobalt (I) species[2] was also unsuccessful in inducing cyclisation of (3a). While AIBN and dibenzoyl peroxide are commonly used in conjunction with other free radical producing species to initiate free-radical chains, they have both been used to generate alkyl radicals directly from alkyl iodides[11,12]. However, when benzene solutions of either of the iodoesters (2a) or (3a) were heated under reflux with AIBN, only starting material was recovered. By contrast, heating of a benzene solution of dibenzoyl peroxide and iodoester (2a) gave the (*E*)-iodomethylene lactone (16a) in 44% yield. Similar treatment transformed a range of iodo acetylenic esters into iodoalkylidene lactones (Table 2).



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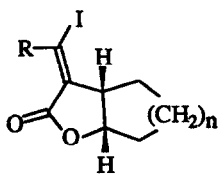
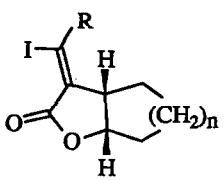


(16) n = 1
(19) n = 2

Table 2. (E)-Iodoalkylidene Lactone Preparations

Lactone	Time (h)	Isolated Yield (%)	Comments
(16a)	7.2	44	
(16b)	2.6	68	
(16c)	2.0	74	
(16d)	5.5	66	
(16e)	2.5	51	(17e),(18) formed also
(16f)	1.1	92	
(19a)	24.0	37	
(19b)	7.5	56	
(19f)	1.7	93	
(19g)	8.0	34	(20g) formed also
(21b)	4.5	94	2:1 *cis*:*trans*
(22b)	2.5	74	1:1 *cis*:*trans*
(23a)	3.0	40	(24) formed also
(23b)	3.5	79	
(25a)	24.0	37	
(25b)	14.0	77	
(26)	3.8	57	
(27)	5.0	33	
(28)	8.8	37	
(29)	3.0	45	
(30)/(31)	5.0	20/22	
(32)/(33)	4.2	20/19	
(34)	20.0	34	



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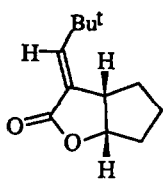
(20) n = 2



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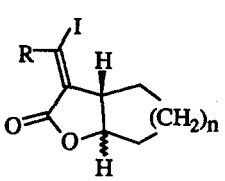

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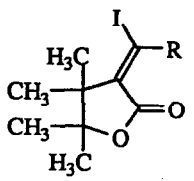

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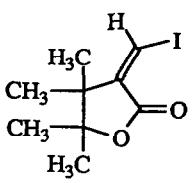

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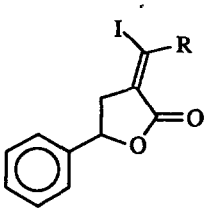

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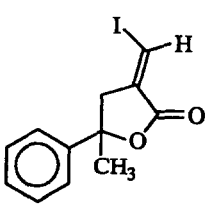

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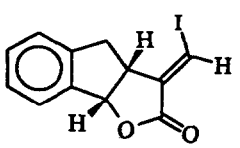

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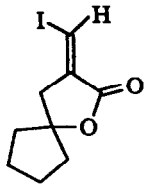

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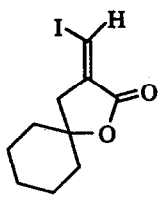

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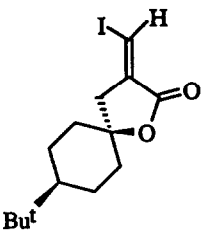

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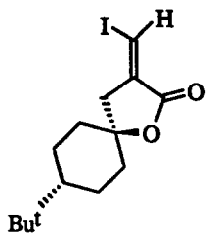

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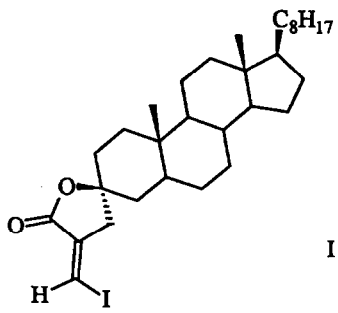

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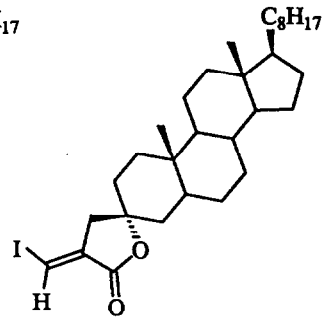

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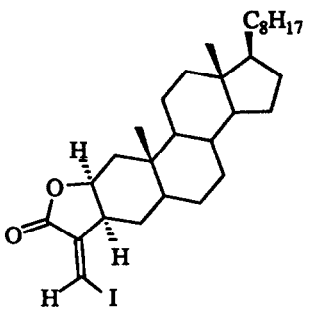
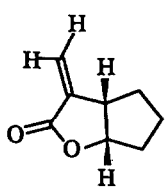


(34)

Iodomethylene lactone (16a) analysed for $C_8H_9IO_2$. Its IR spectrum showed absorption bands typical of a conjugated lactone (1760, 1633 cm^{-1}) and its ^{13}C NMR spectrum showed a carbonyl resonance at δ 166.7 and two alkenyl carbon peaks at 94.8 and 144.2. The high-field position of the alkenyl methine carbon signal (94.8) indicated that the iodine was bound to the β-carbon of the αβ-unsaturated carbonyl system. The remaining carbon signals were in accordance with structure (16a). The ^1H NMR spectrum showed a one-proton doublet (7.79, *J* 2 Hz) as expected for a C=CHI unit, in addition to multiplets for the oxygenated ring junction methine proton (4.99, $W_{h/2}$ 12 Hz) and the allylic ring junction methine proton (3.32, $W_{h/2}$ 20 Hz). This compound has been subsequently converted to the known methylene lactone (35)[2,6,13]. The other iodoalkylidene lactones gave similar spectroscopic data. The indenyl lactone (27) showed a one proton doublet at δ 5.93 (*J* 8 Hz) consistent with benzylic oxygen substitution.

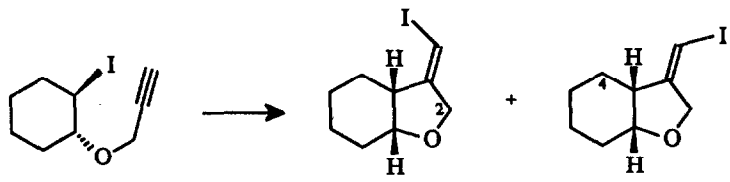


(35)

The products in all cases were the result of 1,5-cyclisation rather than the alternative 1,6. A molecular model of the cyclisation transition state shows that the linearity of the triple bond makes overlap leading to 1,6-cyclisation highly improbable. It has been demonstrated previously that, even in a case where the equivalent alkenyl system cyclises in a 1,6-fashion, alkynyl species react in an exclusively 1,5-manner[14].

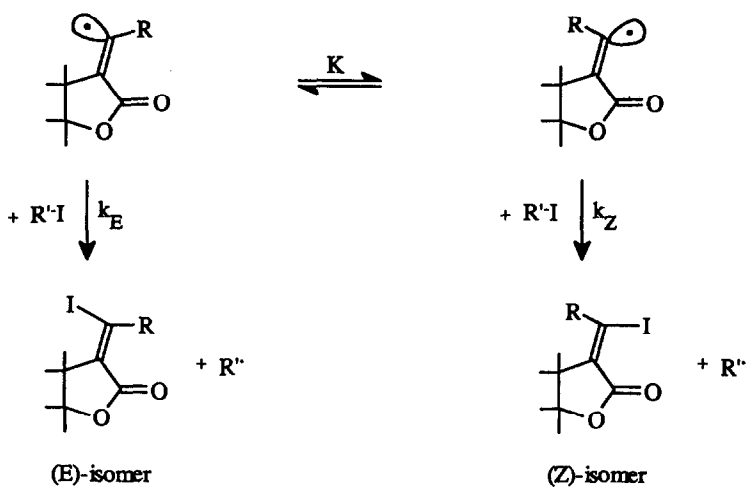
Some of the lactones produced in this study have been isomerised to their (*Z*)-isomers[15]. The (*E*)/(*Z*)-isomeric pairs are readily distinguished by the ^1H NMR chemical shifts of either the vinylic protons or the vinylic alkyl protons. With few exceptions, the formation of the alkylidene grouping in the dibenzoyl peroxide initiated cyclisation was stereospecific giving only the (*E*)-geometric isomer. It is noteworthy that in the absence of a carbonyl grouping, previous studies involving atom transfer cyclisation to triple bonds have given

reaction mixtures containing both (*E*) and (*Z*)-geometric isomers[9]. Likewise, we have isolated a mixture of the (*E*) and (*Z*)-vinyl iodides (37) and (38) from the dibenzoyl peroxide initiated cyclisation of propargyl ether (36).



(36) (37) (38)

The major product (38) had the opposite orientation of the iodine from that obtained by cyclisation of the analogous ester (3a). This was demonstrated by ^{1}H NMR nuclear Overhauser enhancement studies. Irradiation of the vinylic proton signal of (38) (δ 5.90) produced an enhancement of the H-4 peak at δ 2.61. By contrast the equivalent irradiation at δ 5.79 in (37) produced enhancement of the H-2 resonances (δ 4.25, 4.51). It has been well established that vinyl radicals undergo rapid inversion[16] at a rate which is faster than that of the iodine atom transfer process[9]. Thus, in the cyclisation of the iodoesters used in this study, an equilibrium between the (*E*) and (*Z*)-vinyl radicals would be expected to result (Scheme 4). The final ratio of (*E*) and (*Z*)–iodolactones will be controlled by the equilibrium constant, K, and the rates of the atom transfer process, k_E and k_Z.



(E)-isomer (Z)-isomer

Scheme 4

In previous studies on carbocyclic ring systems[9], iodine atom transfer has been shown to occur preferentially to the least hindered side of the vinyl system. This preference is less strong when there are bulky groups at the terminus of the triple bond, an observation which has been attributed to distortion of the equilibrium vinyl radical distribution as a result of steric factors. If steric factors were the sole controlling influence, the acetylenic ester substrates used in this work would be expected to cyclise to give mainly the (*Z*)-isomer. The fact that thermal cyclisation produces mainly the (*E*)-form suggests either that there is a

significant interaction between the carbonyl function and the radical centre which influences the equilibrium vinyl radical distribution, or that there is an interaction between the incoming iodine donor molecule and the carbonyl which reduces k_Z relative to k_E. Studies on the abstraction of iodine from alkyl iodides by carbon centred radicals suggest a transition state with developing anionic character on the carbon from which the iodine is removed[17]. Such a transition state would clearly favour introduction of iodine *trans* to a carbonyl grouping.

The cyclisation of three of the iodo acetylenic esters showed some lack of stereoselectivity, although all favoured the (*E*)-form. The two esters (6a) and (6b) provided an interesting comparison. Compound (6b), with a methyl group on the triple bond, was cyclised solely to the (*E*)-lactone (23b), whereas the ester with a terminal triple bond gave both (*E*) and (Z) products. In both cases, the approach of the iodine atom donor to form the (*E*)-product would be hindered to some extent by the geminal dimethyl grouping at C-4 (Fig 1). This would lower k_E relative to k_Z and could result in the formation of significant amounts of the (Z)-isomer. With the methyl substituted derivative (6b), the path to the (Z)-isomer requires the alkenyl methyl group to come close to the C-4 geminal dimethyls (Fig 2). Presumably this additional interaction helps to preserve the stereoselectivity.

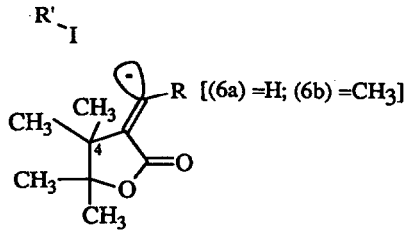


Fig 1

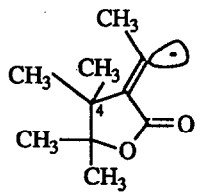


Fig 2

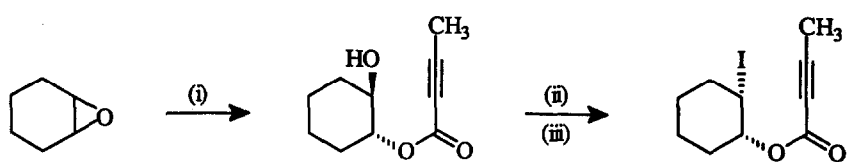
The cyclisation of the cyclopentyl ester (2e) with a *tert*-butyl group on the triple bond is also anomalous. This grouping will encounter steric interactions with either the lactone carbonyl grouping or the methylene grouping of the six-membered ring, depending on the geometry of the vinyl radical. Molecular modelling calculations suggest that the former interaction is the stronger (gas phase strain energies of 112.6 and 103.7 kJ mol^{-1} respectively), thus the equilibrium will be perturbed in favour of an increased production of the (Z)-isomer (17e). The fact that a significant quantity of the iodine free lactone (18) was also identified suggests that both k_E and k_Z have been reduced. By contrast, the trimethylsilyl substituted substrate (2f) cyclised efficiently to give a high yield of the (*E*)-lactone (16f) and no detectable (*Z*)–lactone (17f) (calculated strain energies 91.1 and 91.0 kJ mol-1 for respective vinyl radical intermediates). This reflects the lesser steric demand of the trimethylsilyl group, the result of the longer C-Si bond[18]. The formation of some (Z)-lactone (20g) from the cyclisation of the phenyl substituted substrate (3g) may also be attributed to a change in the equilibrium distribution of the vinyl radicals. In this case it is possibly an electronic repulsion between the phenyl ring and the carbonyl group which is responsible.

The cyclopentyl and cyclohexyl iodo esters cyclised to give lactones with a *cis* ring junction. The more conformationally mobile cycloheptyl and cyclooctyl derivatives gave significant proportions of the *trans*-isomer as well. With the cyclohexyl derivatives, a marked difference in the bandwidths of the ring junction proton resonances was observed in the ^1H NMR spectra. The downfield multiplet was assigned to the proton attached to the oxygenated carbon, while the higher field multiplet was assigned to the other ring

junction proton. This latter signal ($W_{h/2}$ 16-22 Hz) consistently had an appreciably greater bandwidth than the former ($W_{h/2}$ 7-11 Hz), consistent with a *cis* geometry. Calculations show that the formation of a *trans* ring junction in bicyclic systems involving fusion of two five-membered rings is energetically unfavourable[19]. This is borne out by numerous literature examples where cyclopentyl systems form *cis* ring junctions in free-radical cyclisations of this type[20]. In the cyclopentane-fused lactones, the two ring junction proton signals again had significantly different bandwidths ($W_{h/2}$ 17-20 and 12-13 Hz), as expected for pseudo-axial and pseudo-equatorial protons respectively.

In a larger ring, the increased flexibility permits formation of a *trans* ring junction. Both the cycloheptyl (4b) and cyclooctyl (5b) iodo acetylenic esters cyclised to give inseparable mixtures of two isomers. ^{1}H NMR revealed that the cycloheptyl system (21b) was a 2:1 ratio of isomers, while the cyclooctyl derivative (22b) comprised equal amounts of each. Similar chemical shifts for the vinylic methyl resonances showed that the isomerism did not involve the double bond. The additional fact that no nuclear Overhauser enhancements of the ring proton NMR signals could be induced by irradiation of the methyl resonances of either of (21b) or (22b) provided further support that these pairs were isomeric at the ring junction. Assignments of the ring junction and methyl proton NMR resonances of the isomeric mixtures were made by comparison with data reported for the equivalent α-methylene lactones[21,22]. The ring junction proton signals for the cycloheptyl α-methylene lactone have been reported at δ 2.95-3.4 and 4.67 for the *cis*-isomer and 2.45-2.8 and 4.17 for the *trans*. A ^{1}H NMR homonuclear correlation experiment on the iodoethylidene lactone mixture (21b) linked resonances at δ 3.01 and 4.63 (major isomer) and at 2.85 and 4.28 (minor isomer). The major isomer was thus assigned the *cis* stereochemistry. Similar analysis enabled peak assignments for the cyclooctyl mixture (22b).

As expected, the geometry of the starting iodoester was not a deciding factor. *Cis* iodo ester (40) was prepared by reacting cyclohexene oxide with butynoic acid, mesylation of the resulting alcohol (39), and iodide displacement of the mesylate (Scheme 5). As with the *trans* ester (3b), dibenzoyl peroxide induced cyclisation of (40) gave the (Z)-iodoethylidene lactone (19b).



(39) (40)

(i) CH_3-C≡C-COOH; (ii) MsCl/Et_3N; (iii) MgI_2

Scheme 5

In general, the rate of formation of iodoalkylidene lactones was increased by the addition of alkyl or trimethylsilyl groups to the triple bond. Substitution by a phenyl group slowed the reaction. These empirical observations support the view that the iodine atom-transfer step is rate-controlling, as alkyl substitution of the triple bond would be expected to reduce the rate of a cyclisation which involves attack of a nucleophilic alkyl radical on the triple bond LUMO. For the atom transfer step, development of anionic character on the iodine

bearing carbon in the transition state[17] should be enhanced by electron withdrawing groups attached to this carbon, or by electron donors such as alkyl groups on the vinylic radical centre. Furthermore, stabilisation of the alkenyl radical by a phenyl group would retard this step.

Cyclisation of the conformationally mobile alicyclic iodoesters (6), (7) and (8) proceeded smoothly. Results with cyclohexyl derivatives were generally inferior to those obtained with other ring sizes. The cyclohexyl iodoesters have a diequatorial orientation as can be seen from the bandwidths of the ring junction proton signals in their ^{1}H NMR spectra. Molecular models show that cyclisation requires the chair system to flip out of this conformation. Cyclisation is more facile in the more conformationally mobile five, seven and eight-membered ring systems. Formation of the spiro lactone systems (30)/(31) and (32)/(33) showed no preference for attack at either the axial or equatorial positions. This parallels results found with carbocyclic systems[9].

The series of compounds chosen demonstrates that primary, secondary and tertiary alkyl iodides can all be cyclised to form iodovinylidene lactones. A wide variety of alkene types may be accommodated. This range has recently been extended to include enol ethers such as dihydropyran[23].

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 p.p.m. 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. Molecular modelling was carried out with PCMODEL-PI, Version 3.1, Serena Software, Box 3076, Bloomington, IN 47402-3076, United States of America.

Reagents : Unless stated otherwise, the starting materials were reagent grade chemicals from commercial sources. 1-Methylene-4-*t*-butylcyclohexane[24] and 3-methylenecholestane[25] were prepared from the corresponding ketones by a modification of the Wittig reaction[26]. Cholest-2-ene was prepared according to a literature method[27]. A reported synthesis of 2-butynoic acid[28] was also adapted for the synthesis of 2-pentynoic acid[29] and 4-methylpentynoic acid[30] 4,4–Dimethylpentynoic acid[31] was prepared from 3,3-dimethylbutyne by lithiation and reaction with CO_2. Trimethylsilylpropynoic acid was prepared according to literature methods[32,33].

Preparation of Iodoesters

Method A. : N-Iodosuccinimide (0.290 g, 1.3 mmol) was added to a stirred solution of the alkene (1.0 mmol) and the acetylenic acid (or other nucleophile) (2.0 mmol) in dry CH_2Cl_2 (10 ml) cooled to the specified temperature. After the specified reaction time, the reaction mixture was washed with 10% $Na_2S_2O_3$ followed by saturated $NaHCO_3$. The combined aqueous layers were extracted with CH_2Cl_2 and the combined organic extracts were dried ($MgSO_4$). Evaporation of the solvent gave the crude product which was further purified by PLC or by radial chromatography.

Method B. : $I(py)_2BF_4$ (0.745 g, 2.0 mmol) in dry CH_2Cl_2 (6 ml) was added slowly to a stirred solution of the alkene (1 mmol), the acetylenic acid (2.3 mmol) and $BF_3.Et_2O$ (1.1 ml, 8.9 mmol) in dry CH_2Cl_2 (2 ml) at -15°C. After the specified time, the reaction mixture was washed with 10% $Na_2S_2O_3$ followed by saturated $NaHCO_3$. The combined aqueous layers were extracted with CH_2Cl_2 and the combined organic extracts were dried ($MgSO_4$). Evaporation of the solvent, followed by filtration of a CH_2Cl_2 solution through alumina, gave the crude material which was further purified by radial chromatography (40% CH_2Cl_2/hexanes).

The preparations of the following iodoesters are reported according to the convention : method (A or B), alkene (mass, amount), nucleophile used, reaction time, reaction temperature, experimental data.

trans-1-Fluoro-2-iodo-cyclohexane (1). Method B, cyclohexene (0.220 g, 2.7 mmol), no added nucleophile, 1 h, -10°C. Flash chromatography (silica, 20% CH_2Cl_2/hexanes) followed by Kugelrohr distillation (75°C/24 mm) gave (1) as a clear oil (0.350 g, 57%); ^1H NMR : 4.09 (m,1H); 4.54 (broad d, *J* 47 Hz, 1H); Anal. Found : C, 31.8; H, 4.7; Calc. for $C_6H_{10}FI$: C, 31.6; H, 4.4%.

trans-2-Iodocyclopentyl propynoate (2a). Method A, cyclopentene (0.140 g, 2.0 mmol), propynoic acid, 20 min., 0°C. Radial chromatography (25% Et_2O/hexanes) gave (2a) as a clear oil (0.422 g, 78%); distilled 45°C (block)/0.09 mm; IR (film) : 3266, 2122 (C≡CH); 1715, 1231 (ester); ^1H NMR : 2.92 (s, 1H), 4.27 (m, $W_{h/2}$ 15 Hz, 1H); 5.43 (m, $W_{h/2}$ 14 Hz, 1H); ^{13}C NMR : 22.4 (CH_2), 27.4 (CH), 29.3 (CH_2), 36.2 (CH_2), 74.3 (C), 75.1 (CH), 85.7 (CH), 151.4 (C); MS, *m/z* : 264 (M^+); Anal. Found : C, 36.3; H, 3.5; I, 48.3; Calc. for $C_8H_9IO_2$: C, 36.4; H, 3.4; I, 48.1%.

Method B, cyclopentene (0.129 g, 1.9 mmol), 5 min., -15°C, Radial chromatography (25% Et_2O/hexanes) gave (2a) (0.400 g, 80%).

trans-2-Iodocyclopentyl 2-butynoate (2b). Method A, cyclopentene (0.102 g, 1.5 mmol), 2-butynoic acid, 150 min., 20°C. Radial chromatography (25% Et_2O/hexanes) gave (2b) as a clear oil (0.325 g, 78%); distilled 48°C (block)/0.15 mm; mp 30-31°C; IR (film) : 2240 (C≡C), 1713, 1252 (ester); ^1H NMR : 2.00 (s, 3H), 2.33 (m, $W_{h/2}$ 30 Hz, 2H); 4.25 (m, $W_{h/2}$ 12 Hz, 1H); 5.39 (m, $W_{h/2}$ 11 Hz, 1H); ^{13}C NMR : 3.9 (CH_3), 22.5 (CH_2), 28.0 (CH), 29.3 (CH_2), 36.3 (CH_2), 72.2 (C), 85.2 (CH), 86.3 (C), 152.7 (C); MS, *m/z* : 278 (M^+); Anal. Found : C, 39.0; H, 4.0; I, 45.5; Calc. for $C_9H_{11}IO_2$: C, 38.8; H, 4.0; I, 45.6%.

trans-2-Iodocyclopentyl 2-pentynoate (2c). Method A, cyclopentene (0.071 g, 1 mmol), 2-pentynoic acid, 145 min, 20°C. Radial chromatography (25% Et_2O/hexanes) gave (2c) as a clear oil (0.211 g, 72%); distilled 78°C (block)/0.025 mm; IR (film) 2236 (C≡C), 1713, 1248 (ester); ^1H NMR : 1.21 (t, *J* 8 Hz, 3H), 2.35 (q, *J* 8 Hz, 2H), 4.26 (m, $W_{h/2}$ 11 Hz, 1H), 5.39 (m, $W_{h/2}$ 11 Hz, 1H); ^{13}C NMR : 12.5 (CH_2 + CH_3), 22.6 (CH_2), 28.0 (CH), 29.4 (CH_2), 36.4 (CH_2), 72.2 (C), 85.2 (CH), 91.4 (C), 152.8 (C); Anal. Found : C, 41.1; H, 4.4;

I, 43.7; Calc. for $C_{10}H_{13}IO_2$: C, 41.1; H, 4.5; I, 43.4%.

trans-2-Iodocyclopentyl 4-methyl-2-pentynoate (2d). Method A, cyclopentene, (0.070 g, 1 mmol), 4-methyl-2-pentynoic acid, 180 min, 20°C. Radial chromatography (25% Et_2O/hexanes) gave (2d) as a pale yellow oil (0.240 g, 79%); distilled 82°C (block)/0.025 mm; IR (film) 2225 (C≡C), 1711, 1246 (ester); ^1H NMR : 1.25 (d, *J* 7 Hz, 6H), 2.69 (septet, *J* 7 Hz, 1H), 4.27 (m, $W_{h/2}$ 17 Hz, 1H), 5.39 (m, $W_{h/2}$ 9 Hz, 1H); ^{13}C NMR : 20.6 (CH), 21.8 (2 x CH_3), 22.6 (CH_2), 28.1 (CH), 29.4 (CH_2), 36.5 (CH_2), 72.1 (C), 85.2 (CH), 94.9 (C), 153.0 (C); Anal. Found : C, 43.2; H, 4.9; Calc. for $C_{11}H_{15}IO_2$ C, 43.2; H, 4.9%.

trans-2-Iodocyclopentyl 4,4-dimethyl-2-pentynoate (2e). Method A, cyclopentene (0.068 g, 1 mmol), 4,4-dimethyl-2-pentynoic acid, 90 min, 20°C. Radial chromatography (25% Et_2O/hexanes) gave (2e) (0.205 g, 63%); distilled 85°C (block)/0.025 mm; IR (nujol) 2213 (C≡C), 1706, 1267(ester); ^1H NMR : 1.29 (s, 9H), 4.27 (m, $W_{h/2}$ 11 Hz, 1H), 5.39 (m, $W_{h/2}$ 13 Hz, 1H); ^{13}C NMR : 22.6 (CH_2), 27.9 (C), 28.1 (CH), 29.4 (CH_2), 30.0 (3 x CH_3), 36.5 (CH_2), 71.4 (C), 85.2 (CH), 97.2 (C), 153.1 (C); Anal. Found : C, 44.9; H, 5,2; I, 39.9; Calc. for $C_{12}H_{17}IO_2$ C, 44.9; H, 5.3; I, 39.8%.

trans-2-Iodocyclopentyl trimethylsilylpropynoate (2f). Method A, cyclopentene (0.091 g, 1.3 mmol), trimethylsilylpropynoic acid, 2 h, 0°C. Radial chromatography (25% Et_2O/hexanes) gave (2f) as a clear oil (0.290 g, 65%); distilled 45°C (block)/0.04 mm; IR (film) : 2179 (C≡C), 1713, 1221 (ester); ^1H NMR : 0.08 (s, 9H); 2.14 (m, $W_{h/2}$ 24 Hz, 2H), 4.08 (m, $W_{h/2}$ 11 Hz, 1H); 5.22 (m, $W_{h/2}$ 11 Hz, 1H); ^{13}C NMR : 0.9 (CH_3), 22.5 (CH_2), 27.7 (CH), 29.3 (CH_2), 36.3 (CH_2), 85.3 (CH), 94.2 (C), 94.5 (C), 151.8 (C); MS, *m/z* : 336 (M^+). Anal. Found : C, 39.0; H, 5.2; Calc. for $C_{11}H_{17}IO_2Si$: C, 39.3, H; 5.1%.

trans-2-Iodocyclopentyl phenylpropynoate (2g). Method A, cyclopentene (0.350 g, 5 mmol), phenylpropynoic acid, 4 h, 20°C. Radial chromatography (30% ether / hexane) gave (2g) as a yellow oil (1.601 g, 94%); distilled 78°C (block)/0.025 mm; IR (film) 2220 (C≡C), 1707, 1281 (ester) 1489, 758, 688 (phenyl); ^1H NMR: 4.31 (m, $W_{h/2}$ 12 Hz, 1H), 5.47 (m, $W_{h/2}$ 11 Hz, 1H), 7.40 (m, 3H), 7.58 (dd, *J* 7, 1 Hz, 2H); ^{13}C NMR: 22.5 (CH_2), 28.0 (CH), 29.4 (CH_2), 36.4 (CH_2), 80.4 (C), 85.4 (CH), 86.8 (C), 119.4 (C), 128.6 (2 x CH), 130.7 (CH), 133.0 (2 x CH), 152.9 (C); Anal. Found : C, 49.5; H, 3.9; Calc. for $C_{14}H_{13}IO_2$: C, 49.4; H, 3.9%.

trans-2-Iodocyclohexyl propynoate (3a). Method A, cyclohexene (1.26 g, 15.3 mmol), propynoic acid, 2 h, 20°C. Radial chromatography (25% Et_2O/hexanes) gave (3a) as a white solid (3.71 g, 87%); distilled 70°C (block)/0.09 mm; mp 62°C; IR (film); 3299, 2122 (C≡CH), 1710, 1238 (ester); UV : 258 (ε 850); ^1H NMR : 2.10 (s, 1H), 4.07 (ddd, *J* 11, 9, 4 Hz, 1H); 4.95 (ddd, *J* 9, 9, 5 Hz, 1H); ^{13}C NMR : 23.4 (CH_2), 26.7 (CH_2), 29.9 (CH), 31.1 (CH_2), 37.5 (CH_2), 74.7 (C), 75.2 (CH), 78.7 (CH), 151.4 (C); MS, *m/z* : 278 (M^+); Anal. Found : C, 39.1; H, 4.1; I, 46.0; Calc. for $C_9H_{11}IO_2$: C, 38.9; H, 4.0; I, 45.6%.

Method B, cyclohexene (0.160 g, 1.95 mmol), 5 min., -15°C, Radial chromatography (25% Et_2O/hexanes) gave (3a) (0.428 g, 79%).

trans-2-Iodocyclohexyl 2-butynoate (3b). Method A, cyclohexene (0.123 g, 1.5 mmol), 2-butynoic acid, 2 h, 20°C. Radial chromatography (25% Et_2O/hexanes) gave (3b) as a white solid (0.377 g, 86%); distilled

78°C (block)/0.08 mm; mp 66°C; IR (film) : 2241 (C≡C), 1709, 1256 (ester); ^{1}H NMR : 2.02 (s, 3H); 4.09 (ddd, *J* 9, 9, 5 Hz, 1H); 4.99 (ddd, *J* 11, 9, 4 Hz, 1H); ^{13}C NMR : 4.0 (CH_3), 23.5 (CH_2), 26.8 (CH_2), 30.5 (CH), 31.2 (CH_2), 37.6 (CH_2), 72.4 (C), 78.2 (CH), 86.3 (C), 152.6 (C); MS, *m/z* : 292 (M^+); Anal. Found : C, 41.3; H, 4.6; I, 43.6; Calc. for $C_{10}H_{13}IO_2$: C, 41.1; H, 4.5; I, 43.4%.

trans-2-Iodocyclohexyl trimethylsilylpropynoate (3f). Method A, cyclohexene (0.182 g, 2.2 mmol), trimethylsilylpropynoic acid, 2.5 h, 20°C. Radial chromatography (25% Et_2O/hexanes) gave (3f) as a clear oil (0.573 g, 74%); distilled 53°C (block)/0.04 mm; IR (film) : 2180 (C≡C), 1710, 1230 (ester); ^{1}H NMR : 0.09 (s, 9H); 2.27 (m, $W_{h/2}$ 22 Hz, 1H); 3.94 (m, $W_{h/2}$ 24 Hz, 1H), 4.82 (m, $W_{h/2}$ 22 Hz, 1H); ^{13}C NMR : 0.8 (CH_3), 23.4 (CH_2), 26.7 (CH_2), 30.2 (CH), 31.1 (CH_2), 37.5 (CH_2), 78.4 (CH), 94.6 (C), 94.7 (C), 152.0 (C); MS, *m/z* : 350 (M^+); Anal. Found : C, 41.3; H, 5.5; I, 36.5; Calc. for $C_{12}H_{19}IO_2Si$: C, 41.2; H, 5.5; I, 36.2%.

trans-2-Iodocyclohexyl phenylpropynoate (3g). Method A, cyclohexene (0.164 g, 2.0 mmol), phenylpropynoic acid, 80 min., 20°C. Flash chromatography (Al_2O_3, 20% Et_2O/hexanes) gave (3g) as a clear oil (0.515 g, 73%); distilled 78°C (block)/0.02 mm; IR (film) : 3389, 2224 (C≡CH), 3057, 1488, 770, 700 (benzene), 1711, 1283, 1180 (ester); ^{1}H NMR : 4.15 (ddd, *J* 10, 10, 4 Hz, 1H), 5.08 (ddd, 9, 9, 5 Hz, 1H), 7.35-7.49 (m, 3H), 7.61 (d, *J* 5.7 Hz, 2H); ^{13}C NMR : 23.4 (CH_2), 26.7 (CH_2), 30.3 (CH), 31.2 (CH_2), 37.6 (CH_2), 78.4 (CH), 80.7 (C), 86.9 (C), 119.6 (C), 128.6 (2 x CH), 130.8 (CH), 133.1 (2 x CH), 153.0 (C); MS, *m/z* : 354 (M^+); Anal. Found : C, 51.0; H, 4.4; I, 36.0; Calc. for $C_{15}H_{15}IO_2$: C, 50.9; H, 4.3; I, 35.8%.

trans-2-Iodocycloheptyl propynoate (4a). Method A, cycloheptene (0.096 g, 1.0 mmol), propynoic acid, 1 h, 20°C. Radial chromatography (25% Et_2O/hexanes) gave (4a) as a white solid (0.249 g, 85%); distilled 70°C (block)/0.06 mm; mp 62°C; IR (film) : 3285, 2120 (C≡CH), 1713, 1233 (ester); ^{1}H NMR : 2.94 (s, 1H), 4.33 (ddd, *J* 8, 8, 4 Hz, 1H); 5.27 (ddd, *J* 8, 8, 3 Hz, 1H); ^{13}C NMR : 21.9 (CH_2), 26.8 (CH_2), 27.4 (CH_2), 31.2 (CH_2), 34.1 (CH), 36.4 (CH_2), 74.7 (C), 75.1 (CH), 83.4 (CH), 151.3 (C); MS, *m/z* : 292 (M^+); Anal. Found : C, 41.3; H, 4.6; I, 43.4; Calc. for $C_{10}H_{13}IO_2$: C, 41.1; H, 4.5; I, 43.4%.

Method B, cycloheptene (0.180 g, 1.9 mmol), 5 min., -15°C. Radial chromatography (25% Et_2O/hexanes) gave (4a) (0.293 g, 54%).

trans-2-Iodocycloheptyl 2-butynoate (4b). Method A, cycloheptene (0.038 g, 0.40 mmol), 2-butynoic acid, 1 h, 20°C. Flash chromatography (Al_2O_3, 25% Et_2O/hexanes) gave (4b) (0.113 g, 93%); distilled 75°C (block)/0.06 mm; IR (film) : 2170 (C≡C), 1750, 1213 (ester); ^{1}H NMR : 1.98 (s, 3H); 4.28 (ddd, *J* 8, 8, 4 Hz, 1H); 5.19 (ddd, *J* 8, 8, 4 Hz, 1H); ^{13}C NMR; 4.0 (CH_3), 21.8 (CH_2), 26.6 (CH_2), 27.2 (CH_2), 31.1 (CH_2), 34.5 (CH), 36.3 (CH_2), 72.4 (C), 82.7 (CH), 86.1 (C), 152.5 (C); MS, *m/z* : 306 (M^+); Anal. Found : C, 43.2; H, 5.1; I, 41.5, Calc. for $C_{11}H_{15}IO_2$: C,43.2; H, 4.9; I, 41.5%.

trans-2-Iodocyclooctyl propynoate (5a). Method A, cyclooctene (0.112 g, 1.0 mmol), propynoic acid, 1 h, 20°C. Radial chromatography (40% CH_2Cl_2/hexanes) gave (5a) as a white solid (0.265 g, 85%); distilled 75°C (block)/0.07 mm; mp 39°C; IR (film) : 3254, 2118 (C≡CH), 1715, 1237 (ester); ^{1}H NMR : 2.13 (m, $W_{h/2}$ 45 Hz, 2H), 2.93 (s, 1H); 4.42 (ddd, *J* 10, 6, 3 Hz, 1H); 5.32 (ddd, *J* 10, 7, 3 Hz, 1H); ^{13}C NMR : 25.2 (CH_2), 25.4 (CH_2), 26.1 (CH_2), 26.8 (CH_2), 32.5 (CH_2), 32.8 (CH_2), 36.2 (CH), 74.9 (C), 75.1 (CH), 83.1 (CH), 151.7 (C); MS, *m/z* : 306 (M^+). Anal. Found : C, 43.1; H, 4.9; I, 41.4; Calc. for $C_{11}H_{15}IO_2$: C, 43.2; H, 4.9; I,

41.5%.

trans-2-Iodocyclooctyl 2-butynoate (5b). Method A, cyclooctene (0.230 g, 2.1 mmol), 2-butynoic acid, 2 h, 20°C. Radial chromatography (25% Et_2O/hexanes) gave (5b) (0.601 g, 90%); distilled 80°C (block)/0.06 mm; IR (film) : 2250 (C≡C), 1709, 1261 (ester); ^1H NMR : 2.02 (s, 3H), 4.42 (ddd, *J* 10, 6, 3 Hz, 1H), 5.29 (ddd, *J* 10, 8, 2 Hz, 1H); ^{13}C NMR : 4.0 (CH_3), 25.1 (CH_2), 25.4 (CH_2), 26.1 (CH_2), 26.8 (CH_2), 32.5 (CH_2), 32.7 (CH_2), 36.7 (CH), 72.5 (C), 82.3 (CH), 86.1 (C), 152.7 (C); MS, *m/z* : 320 (M^+). Anal. Found : C, 45.2; H, 5.6; I, 39.6; Calc. for $C_{12}H_{17}IO_2$: C, 45.0; H, 5.4; I, 39.6%.

2-Iodo-1,1,2-trimethylpropyl propynoate (6a). Method A, 2,3-dimethyl-2-butene (0.700 g, 10 mmol), propynoic acid, 20 min, 0°C. Radial chromatography (25% Et_2O/hexanes) gave (6a) as unstable, white crystals (1.940 g, 72%); distilled 45°C (block)/0.04 mm; IR (nujol) 2115 (C≡C), 1715, 1256 (ester); ^1H NMR :1.78 (s, 6H), 2.05 (s, 6H), 2.82 (s, 1H); ^{13}C NMR : 22.6 (2 x CH_3), 33.3 (2 x CH_3), 56.7 (C), 72.9 (CH), 75.4 (C), 89.6 (C), 151.2 (C); Anal. Found : C, 38.6; H, 4.6; Calc. for $C_9H_{13}IO_2$: C, 38.6; H, 4.7%.

2-Iodo-1,1,2-trimethylpropyl 2-butynoate (6b). Method A, 2,3-dimethyl-2-butene (0.168 g, 2.0 mmol), 2-butynoic acid, 20 min., -5°C. Radial chromatography (25% Et_2O/hexanes) gave (6b) (0.351 g, 60%); distilled 65°C (block)/0.08 mm; IR (film) : 2250 (C≡C), 1708, 1270 (ester); ^1H NMR : 1.75 (s, 6H); 1.98 (s, 3H); 2.05 (s, 6H); ^{13}C NMR : 3.9 (CH_3), 22.5 (2 x CH_3), 33.2 (CH_3), 33.2 (CH_3), 57.4 (C), 73.3 (C), 83.5 (C), 88.4 (CH), 152.3 (C). Anal. Found : C, 40.9; H, 5.1; I, 43.2; Calc. for $C_{10}H_{15}IO_2$: C, 40.8; H, 5.1; I, 43.2%.

2-Iodo-1-phenylethyl propynoate (7a). Method A, styrene (0.400 g, 3.85 mmol), propynoic acid, 240 min, reflux. Radial chromatography (30% Et_2O/hexanes) gave (7a) as a pale yellow oil (0.800 g, 69%); distilled 90°C (block)/0.032 mm; IR (film) 3276, 1603, 1588, 751, 698 (Ar), 2118 (C≡C), 1714, 1231 (ester); ^1H NMR : 2.94 (s, 1H), 3.45 (dd, *J* 11, 5 Hz, 1H), 3.54 (dd, *J* 11, 8 Hz, 1H), 5.96 (dd, *J* 8, 6 Hz, 1H), 7.36, (s, 5H); ^{13}C NMR : 6.2 (CH_2), 74.1 (C), 75.8 (CH), 77.5 (CH), 126.6 (2 x d), 128.9 (2 x d), 129.2 (CH), 137.3 (C), 151.4 (C); Anal. Found: C, 44.0; H, 2.8; I, 43.0; Calc. for $C_{11}H_9IO_2$ C, 44.0; H, 3.0; I, 42.3%.

2-Iodo-1-phenylethyl 2-butynoate (7b). Method A, styrene (0.208 g, 2.0 mmol), 2-butynoic acid, 4 h, 20°C. Radial chromatography (25% Et_2O/hexanes) gave (7b) as an oil (0.624 g, 99%); distilled 65°C (block)/0.03 mm; IR (film); 3020, 1500, 750, 700 (benzene), 2248 (C≡C), 1710, 1250 (ester); ^1H NMR : 2.01 (s, 3H), 3.46 (dd, *J* 11, 6 Hz, 1H), 3.52 (dd, *J* 11, 8 Hz, 1H), 5.93 (dd, *J* 8, 6 Hz, 1H), 7.37 (s, 5H); ^{13}C NMR : 4.0 (CH_3), 6.7 (CH_2), 72.1 (C), 76.8 (CH); 86.9 (C), 126.6 (2 x CH), 128.8 (2 x CH), 129.0 (CH), 137.7 (C), 152.4 (C); MS, *m/z* : 314 (M^+); Anal. Found : C, 46.0; H, 3.6; I, 40.6; Calc. for $C_{12}H_{11}IO_2$: C, 45.9; H, 3.5; I, 40.4%.

2-Iodo-1-methyl-1-phenylethyl propynoate (8). Method A, 2-phenyl-1-propene (0.591 g, 5.0 mmol), propynoic acid, 210 min., 0°C. Radial chromatography (25% Et_2O/hexanes) gave (8) as an oil (0.752 g, 48%); distilled 130°C (block)/0.03 mm; IR (film) : 3273, 2116 (C≡CH), 1716, 1240 (ester); UV : 243 (ε 5812); ^1H NMR : 1.98 (s, 3H), 2.85 (s, 1H), 3.70 (d, *J* 11 Hz, 1H), 3.79 (d, *J* 11 Hz, 1H), 7.32 (m, 5H); ^{13}C NMR : 16.2 (CH_2), 25.8 (CH_3), 74.2 (CH), 75.0 (C), 83.8 (C), 124.6 (2 x CH), 128.1 (CH), 128.6 (2 x CH), 140.5 (C), 150.5 (C); Anal. Found : C, 46.1; H, 3.7; Calc. for $C_{12}H_{11}IO_2$: C, 45.9; H, 3.5%.

trans-2-Iodo-2,3-dihydroindenyl propynoate (9). Method A, indene (0.116 g, 1.0 mmol), propynoic acid, 20 min., 60°C. Radial chromatography (25 Et_2O/hexanes) gave (9) as a white solid (0.260 g, 83%); distilled 95°C (block)/0.06 mm; mp 90°C; IR (film); 3277, 2118 (C≡CH), 1713, 1211 (ester); ^1H NMR : 2.93 (s, 1H), 3.34 (dd, *J* 17, 4 Hz, 1H), 3.81 (dd, *J* 17, 7 Hz, 1H), 4.57 (ddd, *J* 7, 4, 3 Hz, 1H), 6.45 (d, *J* 3 Hz, 1H); ^{13}C NMR : 23.3 (CH), 43.6 (CH_2), 74.2 (C), 75.8 (CH), 87.6 (CH), 124.9 (CH), 126.3 (CH), 127.7 (CH), 130.1 (CH), 137.2 (C), 142.3 (C), 151.6 (C); Mass spectrum *m/z* : 312 (M^+); Anal. Found : C, 46.0; H, 2.8; I, 40.4; Calc. for $C_{12}H_9IO_2$: C, 46.2; H, 2.9; I, 40.7%.

1-(Iodomethyl)cyclopentyl propynoate (10). Method A, methylenecyclopentane (0.460 g, 5.6 mmol), propynoic acid, 120 min., 0°C. Radial chromatography (25% Et_2O/hexanes) gave (10) as an oil (0.812 g, 52%); distilled 55°C (block)/0.03 mm; IR (film) : 3281, 2118 (C≡CH), 1698, 1240 (ester); UV : 251 (ε 628); ^1H NMR : 2.26 (m, $W_{h/2}$ 26 Hz, 2H), 2.88 (s, 1H), 3.79 (s, 2H); ^{13}C NMR : 12.4 (CH_2), 24.4 (CH_2), 38.0 (CH_2), 73.8 (CH), 75.3 (C), 92.7 (C), 151.6 (C); Anal. Found : C, 38.8; H, 4.1, I, 45.7; Calc. for $C_9H_{11}IO_2$: C, 38.9; H, 4.0; I, 45.6%.

1-(Iodomethyl)cyclohexyl propynoate (11). Method A, methylenecyclohexane (0.52 g, 5.4 mmol), propynoic acid, 2 h, 0°C. Radial chromatography (25% Et_2O/hexanes) gave (11) (0.52 g, 33%); distilled 75°C (block)/0.06 mm; IR (film) : 3280, 2115 (C≡CH); 1711 (ester); UV : 255 (ε 1941); ^1H NMR (200 MHz) : 1.25 (br s, 1H); 1.53 (m, $W_{h/2}$ 18 Hz, 7H); 2.33 (m, $W_{h/2}$ 20 Hz, 2H); 2.84 (s, 1H); 3.74 (s, 2H); ^{13}C NMR (50 MHz) : 13.9 (CH_2); 22.0 (CH_2); 25.1 (CH_2); 34.3 (CH_2); 73.4 (CH); 75.4 (C); 83.7 (C); 151.3 (C); Anal. Found : C, 41.5; H, 4.3; Calc. for $C_{10}H_{13}IO_2$: C, 41.1; H, 4.4%.

cis and trans-1-(Iodomethyl)-4-t-butylcyclohexyl propynoate (12). Method A, 1-methylene-4-*t*-butylcyclohexane (3.08 g, 19.3 mmol), propynoic acid, 5.2 h, 0°C. Radial chromatography (25% Et_2O/hexanes) gave an isomeric mixture (ratio 1:2.3) of (12) (0.780 g, 11%); distilled 85°C (block)/0.05 mm; IR (film) : 3284, 2119 (C≡CH); 1713 (ester); ^1H NMR (200 MHz), isomer with axial CH_2I : 0.86 (s, 9H); 2.86 (s, 1H); 3.90 (s, 2H); isomer with equatorial CH_2I : 0.87 (s, 9H); 2.87 (s, 1H); 3.70 (s, 2H); ^{13}C NMR (50 MHz), isomer with axial CH_2I : 10.8 (CH_2); 23.9 (CH_2); 27.5 (CH_3); 32.2 (C); 34.5 (CH_2); 47.2 (CH); 73.4 (CH); 75.5 (C); 84.7 (C); 151.2 (C); isomer with equatorial CH_2I : 14.2 (CH_2); 22.5 (CH_2); 27.5 (CH_3); 32.2 (C); 34.5 (CH_2); 46.9 (CH); 73.4 (CH); 75.3 (C); 83.1 (C); 151.3 (C);; Anal. Found : C, 47.8; H, 5.9; Calc. for $C_{14}H_{21}IO_2$: C, 48.2; H, 6.0%.

3-Iodomethyl-5α-cholestan-3-yl propynoate (13). Method A, 3-methylenecholestane (2.19 g, 5.6 mmol), propynoic acid, 3.25 h, 0°C. Radial chromatography (25% Et_2O/hexanes) gave an isomeric mixture (ratio 1:3.5) of (13) (0.95 g, 29%); IR (film) : 3301, 2119 (C≡CH); 1713 (ester); ^1H NMR (200 MHz) : 0.64 (s, 3H); 0.77 (s, 3H); 0.86 (d, *J* 6 Hz, 12H); 0.89 (d, *J* 7 Hz, 6H); 0.95 (s, 3H); 0.98 (s, 3H); 2.82 (s, 1H, major); 2.85 (s, 1H, minor); 3.70 (s, 2H, minor); 3.94 (s, 2H, major). This was used without further purification.

3α-Iodocholestan-2β-yl propynoate (14). Method A, cholest-2-ene (0.190 g, 0.5 mmol), propynoic acid, 480 min, 20°C. Radial chromatography (25% Et_2O/hexanes) gave (14) (0.220 g, 78%); IR (nujol) 2119 (C≡C), 1714, 1225 (ester); ^1H NMR : 0.64 (s, 3H), 0.84 (s, 3H), 0.88 (s, 3H), 0.95 (s, 3H), 2.88 (s, 1H), 4.58 (m, $W_{h/2}$ 16 Hz, 1H), 5.30 (m, $W_{h/2}$ 15 Hz, 1H); ^{13}C NMR : 12.2 (CH_3), 14.8 (CH_3), 18.8 (CH_3), 21.1 (CH_2); 22.8 (CH_3),

23.1 (CH_3), 24.2 (CH_2), 24.4 (CH_2), 27.5 (CH_2), 28.1 (CH), 28.3 (CH_2), 29.7 (CH), 31.8 (CH_2), 33.8 (CH_2), 35.0 (d + s), 35.9 (CH), 36.2 (CH_2), 36.3 (CH_2), 39.6 (CH_2), 40.0 (CH_2), 41.9 (CH), 42.7 (C), 54.8 (CH), 56.4 (2 x d), 74.5 (C), 75.0 (CH), 77.1 (CH), 151.4 (C); Anal. Found: C, 63.4; H, 8.1; I, 22.4; Calc. for $C_{30}H_{47}IO_2$ C, 63.6; H, 8.4; I, 22.4%.

trans-2-Iodocyclohexyl propanoate (15). Method B, cyclohexene (0.300 g, 3.6 mmol), propanoic acid, 5 min., -20°C. Radial chromatography (40% CH_2Cl_2/hexanes) gave (15) as an oil (0.400 g, 39%); distilled 54°C (block)/0.6 mm; IR (film) : 1734, 1181 (ester); ^{1}H NMR : 1.18 (t, *J* 7 Hz, 3H), 2.36 (q, *J* 7 Hz, 2H), 4.07 (ddd, *J* 9, 9, 4 Hz, 1H), 4.88 (ddd, *J* 10, 9, 4 Hz, 1H); ^{13}C NMR : 9.2 (CH_3), 23.6 (CH_2), 27.1 (CH_2), 27.9 (CH_2), 31.6 (CH_2), 31.9 (CH), 37.9 (CH_2), 76.5 (CH), 173.3 (C); Anal. Found : C, 38.0; H, 5.5; I, 44.7; Calc. for $C_9H_{15}IO_2$: C, 38.3; H, 5.4; I, 45.0%.

trans-1-(2-Propynyloxy)-2-iodocylohexane (36). Method A, cyclohexene (0.160 g, 1.9 mmol), propargyl alcohol, 180 min reflux. PLC (25% ether/hexanes) gave (36) as a pale yellow oil (0.350 g, 88%); distilled 90°C (block)/0.07 mm; IR (film) : 3291, 2150 (C≡CH), 1100 (C-O); ^{1}H NMR : 2.43 (t, *J* 2 Hz, 1H), 3.57 (ddd, *J* 8, 8, 4 Hz, 1H), 4.10 (m, $W_{h/2}$ 24 Hz, 1H), 4.28 (d, *J* 2 Hz, 2H); ^{13}C NMR : 23.5 (CH_2), 26.9 (CH_2), 31.1 (CH_2), 34.7 (CH), 37.6 (CH_2), 56.8 (CH_2), 74.3 (CH), 80.1 (C), 81.8 (CH); MS *m/z* 264.0000; Calc. for $C_9H_{13}IO$: 264.0011.

trans-2-Hydroxycyclohexyl 2-butynoate (39)

A solution of cyclohexene oxide (0.250 g, 2.55 mmol) and 2-butynoic acid (0.250 g, 2.98 mmol) in dry $CHCl_3$ (10 ml) was heated under reflux for 8 h. The reaction mixture was cooled, poured into $NaHCO_3$ (10%, 50 ml) and extracted with CH_2Cl_2 (2 x 50 ml). The organic extracts were dried over anhydrous $MgSO_4$ and the solvent removed to give the crude alcohol which was recrystallised from hexane to give pure (39) as white needles (0.200 g, 43%); mp 85°C; IR (film) : 3417 (OH), 2242 (C≡C), 1707, 1259 (ester); ^{1}H NMR : 2.00 (s, 3H), 3.60 (m, $W_{h/2}$ 20 Hz, 1H), 4.65 (m, $W_{h/2}$ 21 Hz, 1H); ^{13}C NMR : 3.7 (CH_3), 23.6 (CH_2), 23.7 (CH_2), 29.6 (CH_2), 32.7 (CH_2), 72.0 (CH), 72.5 (C), 79.6 (CH), 85.8 (C), 153.5 (C); Anal. Found: C, 65.8; H, 7.7; Calc. for $C_{10}H_{14}O_3$: C, 65.9; H, 7.7%.

cis-2-Iodocyclohexyl 2-butynoate (40)

A solution of triethylamine (2.170 g, 20.2 mmol), mesyl chloride (0.444 g, 3.1 mmol) and (39) (0.200 g, 1.1 mmol) in dry CH_2Cl_2 (50 ml) was stirred at room temperature for 36 h. The solution was washed with HCl (10%, 50 ml), saturated $NaHCO_3$ (50 ml), and brine (50 ml), then dried over anhydrous $MgSO_4$. Removal of the solvent gave the crude mesylate (0.240 g); IR (film) : 2243 (C≡C), 1704, 1261 (ester), 1361, 1174 (mesylate); ^{1}H NMR : 2.00 (s, 3H), 3.06 (s, 3H), 4.54 (m, $W_{h/2}$ 27 Hz, 1H), 4.86 (m, $W_{h/2}$ 21 Hz, 1H); ^{13}C NMR : 3.8 (CH_3), 23.0 (CH_2), 23.3 (CH_2), 30.0 (CH_2), 31.8 (CH_2), 38.3 (CH_3), 72.0 (C), 74.7 (CH), 81.6 (CH), 86.7 (C), 152.5 (C).

Iodine (1.020 g, 4.0 mmol) was added to a stirred suspension of magnesium turnings (0.240 g, 10.0 mmol) in anhydrous ether under a nitrogen atmosphere. Stirring was continued until the iodine colour had dissipated. The ethereal magnesium iodide solution was transferred to a solution of the crude mesylate (0.240 g) in CH_2Cl_2 (5 ml) and the mixture was heated under reflux in a nitrogen atmosphere for 6 h. Iced water (20 ml) was added and the aqueous layer was extracted with CH_2Cl_2 (2 x 20 ml). The combined organic

extracts were washed with $Na_2S_2O_3$ (10%, 50 ml) then dried over anhydrous $MgSO_4$. Removal of the solvent followed by PLC (25% $CHCl_3/C_6H_6$) gave iodoester (40) (0.060 g, 23%); distilled 50°C (block)/0.15 mm; IR (film): 2241 (C≡C), 1708, 1252 (ester); ^{1}H NMR : 2.02 (s, 3H) 4.42 (m, $W_{h/2}$ 18 Hz, 1H), 4.63 (m, $W_{h/2}$ 12 Hz, 1H); ^{13}C NMR : 6.6 (CH_3), 24.8 (CH_2), 26.3 (CH_2), 31.7 (CH_2), 36.9 (CH_2), 37.1 (CH), 75.0 (C), 77.2 (CH), 88.8 (C), 155.4 (C). Anal. Found: C, 41.2; H, 4.4; Calc. for $C_{10}H_{13}IO_2$ C, 41.1; H, 4.5%. MS *m/z* 291.9960; Calc. for $C_{10}H_{13}IO_2$: 291.9962.

Attempted Cyclisations with Tri-n-butyltin Hydride

(a) A solution of tri-n-butyltin hydride (0.230 g, 0.79 mmol) and azobisisobutyronitrile (0.005 g, 0.030 mmol) in C_6H_6 (4 ml) was added to a boiling solution of iodoester (3a) (0.130 g, 0.47 mmol) in C_6H_6 (5 ml). After the mixture had been heated under reflux for 3 h, the solvent was removed. The residue was dissolved in Et_2O (25 ml) and washed with 10% aqueous KF (20 ml). The organic layer was dried ($MgSO_4$) and the Et_2O removed. TLC and ^{1}H NMR showed only starting material.

(b) Sodium borohydride (0.045 g, 1.19 mmol) was added to a stirred solution of (3a) (0.25 g, 0.90 mmol) and tributyltin chloride (0.070 g, 0.22 mmol) in ethanol (4 ml). The system was then irradiated with a medium pressure Hanovia lamp for 80 min. The mixture was taken up in Et_2O and washed with saturated $NaHCO_3$, 10% KF and the organic phase dried ($MgSO_4$). Evaporation of the solvent gave a light yellow oil (0.150 g) which was identified as 2-iodocyclohexyl propanoate (15) by comparison with an authentic sample (TLC, ^{1}H NMR).

(c) A solution of tributyltin hydride (0.125 g, 0.43 mmol) and dibenzoyl peroxide (0.015 g, 0.062 mmol) in C_6H_6 (3 ml) was added slowly to a boiling solution of (3a) (0.100 g, 0.36 mmol) in dry C_6H_6 (2 ml) over a 3 h period. Evaporation of the solvent gave a residue which TLC and ^{1}H NMR showed to contain mostly starting material with a trace of the (*E*)-iodomethylene lactone (17a).

(d) A stirred solution of (3b) (0.150 g, 0.51 mmol), tributyltin hydride (0.180 g, 0.62 mmol) and azobisisobutyronitrile (0.010 g, 0.061 mmol) in dry C_6H_6 (2 ml) was heated under reflux. After 150 min a further portion of azobisisobutyronitrile (0.010 g) was added and heating was continued for 400 min. The solvent was removed and the residue was dissolved in Et_2O (20 ml). The ethereal layer was shaken with 10 % aqueous KF (10 ml). Separation of the ethereal layer followed by drying ($MgSO_4$), removal of solvent and PLC (25 % Et_2O/hexanes) gave an oil (0.119 g). ^{1}H NMR indicated a 3:1 mixture of starting material and the (*E*)-iodoethylidene lactone (19b).

Dibenzoyl Peroxide Induced Cyclisations

A solution of the iodo acetylenic ester and dibenzoyl peroxide in C_6H_6 was heated under reflux for the specified time. After evaporation of the solvent, the resulting mixture was purified by PLC or by radial chromatography.

The cyclisation reactions are reported according to the convention : iodoester (mass, amount), initiator (mass, amount), volume of C_6H_6, reaction time, experimental data.

(3E,3aα,6aα)-Hexahydro-3-iodomethylene-2H-cyclopenta[b]furan-2-one (16a). (2a) (0.210 g, 0.80 mmol), dibenzoyl peroxide (0.04 g, 0.17 mmol), 2 ml, 7.2 h. Radial chromatography (25% Et_2O/hexanes) gave (16a) (0.092 g, 44%); distilled 80°C (block)/2 mm; IR (film) : 3070, 1633 (C=CH), 1760, 1265 (lactone) ; UV : 252 (ε 8040); ^{1}H NMR : 3.32 (m, $W_{h/2}$ 20 Hz, 1H); 4.99 (m, $W_{h/2}$ 12 Hz, 1H); 7.79 (d, *J* 2 Hz, 1H); ^{13}C NMR : 23.3 (CH_2), 32.4 (CH_2), 34.2 (CH_2), 47.0 (CH), 83.0 (CH), 94.8 (CH), 144.2 (C), 166.7 (C); MS, *m/z* : 264

(M^+); Anal. Found : C, 36.7; H, 3.4; I, 48.4; Calc. for $C_8H_9IO_2$: C, 36.4; H, 3.4; I, 48.1%;

(3E,3aα,6aα)-Hexahydro-3-(1-iodoethylidene)-2H-cyclopenta[b]furan-2-one (16b). (2b) (0.250 g, 0.90 mmol), dibenzoyl peroxide (0.020 g, 0.082 mmol), 2 ml, 2.6 h. PLC (25% Et_2O/hexanes) gave (16b) (0.170 g, 68%); distilled 50°C (block)/0.5 mm; IR (film) : 1753, 1220 (lactone), 1641 (C=C); UV : 254 (ε 11300); ^1H NMR : 3.12 (d, *J* 2 Hz, 3H); 3.37 (m, $W_{h/2}$ 15 Hz, 1H); 4.90 (m, $W_{h/2}$ 11 Hz, 1H); ^{13}C NMR : 23.1 (CH_2), 30.5 (CH_3), 33.5 (CH_2), 34.4 (CH_2), 51.8 (CH), 81.3 (CH), 120.1 (C), 136.9 (C), 165.2 (C); MS, *m/z* : 278 (M^+); Anal. Found : C, 38.8; H, 4.0; I, 45.6; Calc. for $C_9H_{11}IO_2$: C, 38.9; H, 4.0; I, 45.6%.

(3E,3aα,6aα)-Hexahydro-3-(1-iodopropylidene)-2H-cyclopenta[b]furan-2-one (16c). (2c) (0.198 g, 0.68 mmol), dibenzoyl peroxide (0.034 g, 0.14 mmol), 2 ml, 2 h. PLC (25% $CHCl_3/C_6H_6$) gave (16c) as a pale yellow oil (0.147 g, 74 %); distilled 66°C (block)/0.03 mm; IR ($CHCl_3$) 1739.8 (C=O), 1629.8 (C=C); UV : 254 (ε 8312); ^1H NMR :1.12 (t, *J* 7 Hz, 3H), 3.35 (m, $W_{h/2}$ 21 Hz, 3H), 4.89 (m, $W_{h/2}$ 14 Hz, 3H); ^{13}C NMR : 15.0 (CH_3), 23.1 (CH_2), 33.7 (CH_2), 34.5 (CH_2), 34.6 (CH_2), 52.1 (CH), 81.5 (CH), 131.7 (C), 136.2 (C), 164.9 (C); Anal. Found: C, 41.2; H, 4.5; I, 43.2; Calc. for $C_{10}H_{13}IO_2$ C, 41.1; H, 4.5;I, 43.4%.

(3E,3aα,6aα)-Hexahydro-3-(1-iodo-2-methylpropylidene)-2H-cyclopenta[b]furan-2-one (16d). (2d) (0.337 g, 1.10 mmol), dibenzoyl peroxide (0.051 g, 0.21 mmol), 2 ml, 5.5 h. Radial chromatography (25% Et_2O/hexanes) gave (16d) as a pale yellow oil (0.222 g, 66%); distilled 77°C (block)/0.03 mm; IR ($CHCl_3$) 1739.8 (C=O), 1620.2 (C=C); UV : 255 (ε 8776); ^1H NMR : 0.97 (d, *J* 6 Hz, 3H), 0.98 (d, *J* 6 Hz, 3H), 3.39 (m, $W_{h/2}$ 17 Hz, 1H), 3.96 (septet, *J* 6 Hz, 1H), 4.89 (m, $W_{h/2}$ 15 Hz, 1H); ^{13}C NMR : 23.1 (CH_2), 24.0 (CH_3), 24.8 (CH_3), 32.8 (CH), 33.8 (CH_2), 34.5 (CH_2), 52.4 (CH), 81.6 (CH), 134.4 (C), 144.2 (C), 165.0 (C); Anal. Found: C, 43.6; H, 4.8; Calc. for $C_{11}H_{15}IO_2C$, 43.2; H, 4.9%.

(3E,3aα,6aα)-Hexahydro-3-(1-iodo-2,2-dimethylpropylidene)-2H-cyclopenta[b]furan-2-one (16e). (2e) (0.220 g, 0.68 mmol), dibenzoyl peroxide (0.042 g, 0.17 mmol), 2 ml, 2.5 h. Radial chromatography (25% Et_2O/hexanes) gave : (i) unchanged iodoester (2e) (0.019 g, 9%); (ii) (16e) as a pale yellow oil (0.112 g, 51%); distilled 80°C (block)/0.03 mm; IR ($CHCl_3$) 1743.6 (C=O), 1577.8 (C=C); UV : 264 (ε 6261); ^1H NMR : 1.47 (s, 9H), 3.53 (m, $W_{h/2}$ 20 Hz, 1H), 4.84 (m, $W_{h/2}$ 14 Hz, 1H); ^{13}C NMR : 23.0 (CH_2), 32.4 (3 x CH_3), 33.9 (CH_2), 34.3 (CH_2), 41.8 (C), 58.1 (CH), 80.4 (CH), 138.1 (C), 144.6 (C), 163.4 (C); MS, *m/z* 320.0273; Calc. for $C_{12}H_{17}IO_2$ 320.0275; (iii) a 1:1 mixture (^1H NMR) of (*Z*)-iodolactone (17e) and *E*-alkylidene lactone (18)[6] in a 1:1 ratio (0.020 g). These substances were identified by comparison of their ^1H NMR spectra with those of authentic samples.

(3E,3aα,6aα)-Hexahydro-3-[iodo(trimethylsilyl)methylene]-2H- cyclopenta[b]furan-2-one (16f). (2f) (0.309 g, 0.92 mmol), dibenzoyl peroxide (0.025 g, 0.103 mmol), 2 ml, 1.1 h. Radial chromatography (25% Et_2O/hexanes) gave (16f) (0.285 g, 92%) as an oil; distilled 50°C (block)/0.02 mm; IR (film) : 1750, 1210 (lactone), 1590 (C=C); UV : 266 (ε 4030); ^1H NMR : 0.34 (s, 9H); 2.18 (m, $W_{h/2}$ 22 Hz, 1H), 3.43 (ddd, *J* 9, 6, 3 Hz, 1H), 4.96 (m, $W_{h/2}$ 13 Hz, 1H); ^{13}C NMR 1.6 (3 x CH_3), 23.2 (CH_2), 33.1 (CH_2), 34.4 (CH_2), 54.4 (CH), 81.9 (CH), 131.9 (C), 151.0 (C), 165.1 (C); MS, *m/z* 336.0045 (M^+); Calc. for $C_{11}H_{17}IO_2Si$: 336.0043.

(3E,3aα,7aα)-Hexahydro-3-iodomethylene-2(3H)-benzofuranone (19a). (3a) (0.271 g, 0.97 mmol), dibenzoyl peroxide (0.025 g, 0.103 mmol), 2 ml, 24 h. PLC. (25% Et_2O/hexanes) gave (19a) (0.101 g, 37%); distilled 55°C (block)/0.03 mm; IR (film) : 3056, 1633 (C=CH), 1745, 1255 (lactone); UV : 252 (ε 6580); ^1H NMR : 2.98 (m, $W_{h/2}$ 11 Hz, 1H), 4.52 (m, $W_{h/2}$ 15 Hz, 1H), 7.59 (d, *J* 2 Hz, 1H); ^{13}C NMR : 19.3 (CH_2), 22.4 (CH_2), 24.9 (CH_2), 27.1 (CH_2), 43.3 (CH), 75.9 (CH), 90.7 (CH), 146.4 (C), 166.7 (C); MS, *m/z* : 278 (M^+); Anal. Found : C, 38.9; H, 4.0; I, 45.5; Calc. for $C_9H_{11}IO_2$: C, 38.9; H, 4.0; I, 45.6%.

(3E,3aα,7aα)-Hexahydro-3-(1-iodoethylidene)-2(3H)-benzofuranone (19b).

(a) From Trans Ester : (3b) (0.282 g, 0.97 mmol), dibenzoyl peroxide (0.020 g, 0.082 mmol), 2 ml, 7.5 h. PLC (25% CH_2Cl_2/C_6H_6) gave (19b) (0.157 g, 56%); distilled 75°C (block)/0.2 mm; IR (film) : 1750, 1205 (lactone), 1645 (C=C); UV : 253 (ε 6580); ^1H NMR : 2.93 (m, $W_{h/2}$ 20 Hz, 1H); 3.05 (d, *J* 1 Hz, 3H), 4.48 (m, $W_{h/2}$ 7 Hz, 1H); ^{13}C NMR : 19.4 (CH_2), 22.7 (CH_2), 25.1 (CH_2), 27.1 (CH_2), 30.5 (CH_2), 48.4 (CH), 74.9 (CH), 115.1 (C), 139.5 (C), 165.2 (C); MS, *m/z* : 292 (M^+); Anal. Found : C, 41.0; H, 4.5; I, 43.1, Calc. for $C_{10}H_{13}IO_2$: C, 41.1; H, 4.5; I, 43.4%.

(b) From Cis Ester : (40) (0.060 g, 0.21 mmol), dibenzoyl peroxide (0.015 g, 0.061 mmol), 1 ml, 4 h. PLC (25% CH_2Cl_2/C_6H_6) gave (19b) (0.0.021 g, 35%).

(3E,3aα,7aα)-Hexahydro-3-(iodo(trimethylsilyl)methylene)-2(3H)-benzofuranone (19f). (3f) (0.320 g, 0.91 mmol), dibenzoyl peroxide (0.025 g, 0.10 mmol), 2 ml, 1.7 h. PLC (25% Et_2O/hexanes) gave (19f) as an oil (0.296 g, 93%); distilled 50°C (block)/0.02 mm; IR (film) : 1757, 1202 (lactone), 1597 (C=C); UV : 265 (ε 8590); ^1H NMR : 0.08 (s, 9H), 2.26 (m, $W_{h/2}$ 22 Hz, 1H), 3.93 (m, $W_{h/2}$ 25 Hz, 1H), 4.81 (m, $W_{h/2}$ 15 Hz, 1H); ^{13}C NMR : 1.32 (3 x CH_3), 19.4 (CH_2), 22.7 (CH_2), 24.2 (CH_2), 27.1 (CH_2), 51.1 (CH), 75.1 (CH), 127.0 (C), 152.9 (C), 165.0 (C); MS, *m/z* : 350 (M^+); Anal. Found : C,41.3; H, 5.7; I, 36.2; Calc. for $C_{12}H_{19}IO_2Si$: C, 41.2, H; 5.5, I; 36.2%.

(3E,3aα,7aα)- and (3Z,3aα,7aα)-Hexahydro-3-(1-iodobenzylidene)-2(3H)-benzofuranone (19g) and (20g) . (3g) (0.300 g, 0.71 mmol), dibenzoyl peroxide (0.025 g, 0.10 mmol), 2 ml, 8.0 h. PLC (25% Et_2O/hexanes) gave (i) recovered (3g) (0.128 g) (ii) A mixture of (19g) and (20g) (0.101 g, 34%); MS, *m/z* : 354 (M^+). Anal. Found : C, 50.8; H, 4.0; I, 35.5; Calc. for $C_{15}H_{15}IO_2$: C, 50.9; H, 4.3; I, 35.8%. Multiple run PLC (25% Et_2O/hexanes) gave mixtures of (19g) and (20g) which were enriched in either of the two isomers. These enabled deduction of the following spectral parameters. (*E*)-isomer (19g) : IR (CCl_4) : 1765, 1200, 1190 (lactone); UV : 250 (ε 5140); ^1H n.m.r : 2.89 (m, $W_{h/2}$ 22 Hz, 1H), 4.38 (m, $W_{h/2}$ 11 Hz, 1H), 7.32 (s, 5H); ^{13}C NMR : 19.4 (CH_2), 22.7 (CH_2), 24.9 (CH_2), 27.1 (CH_2), 49.2 (CH), 74.5 (CH), 113.9 (C), 127.9 (2 x CH), 128.1 (2 x CH), 129.3 (CH), 140.8 (C), 141.5 (C), 163.6 (C); MS, *m/z* : 354 (M^+). (*Z*)-isomer (20g) : IR (CCl_4) : 1765 (lactone); UV : 261 (ε 4100); ^1H NMR : 3.09 (m, $W_{h/2}$ 23, 1H), 4.59 (m, $W_{h/2}$ 10 Hz, 1H), 7.34 (m, 5H); ^{13}C NMR : 19.0 (CH_2), 22.9 (CH_2), 26.9 (CH_2), 27.3 (CH_2), 43.0 (CH), 74.6 (CH), 103.8 (C), 127.0 (2 x d), 128.3 (2 x d), 129.0 (CH), 139.4 (C), 143.8 (C), 168.8 (C).

(3E,3aα,8aα) and (3E,3aα,8aβ)-Octahydro-3-iodomethylene-2H-cyclohepta[b]furan-2-one (21b). (4b) (0.185 g, 0.6 mmol), dibenzoyl peroxide (0.020 g, 0.10 mmol), 2 ml, 4.5 h. PLC (25% CH_2Cl_2/C_6H_6) the *cis/trans* isomers (21b) in a 2:1 ratio (0.173 g, 94%); IR (film) :1750, 1210 (lactone), 1634 (C=C); UV : 253 (ε 8620); ^1H NMR : *cis* isomer : 3.01 (m, $W_{h/2}$ 32 Hz, 1H), 3.11 (d, *J* 1 Hz, 3H), 4.63 (m, $W_{h/2}$ 24 Hz, 1H);

trans isomer : 2.85 (m, $W_{h/2}$ 29 Hz, 1H), 3.21 (d, *J* 3 Hz, 3H), 4.28 (m, $W_{h/2}$ 24 Hz, 1H); *cis* : *trans* = 2 : 1; ^{13}C NMR : *cis* isomer : 22.1 (CH_2), 27.9 (CH_2), 29.2 (CH_2), 30.6 (CH_2), 30.7 (CH_3), 31.2 (CH_2), 53.7 (CH), 78.8 (CH), 118.7 (C), 137.3 (C), 164.5 (C); *trans* isomer : 24.5 (CH_2), 25.1 (CH_2), 26.9 (CH_2), 29.2 (CH_2), 32.4 (CH_2), 32.5 (CH_3), 49.4 (CH), 81.3 (CH), 127.4 (C), 130.2 (C), 165.8 (C); MS, *m/z* : 306 (M^+); Anal. Found : C, 43.2; H, 5.1 ; Calc. for $C_{11}H_{15}IO_2$: C, 43.2; H, 4.9%.

(3E,3aα,9aα) and (3E,3aα,9aβ)-Octahydro-3-Iodomethylenecycloocta[b]furan-2(3H)-one (22b). (5b) (0.239 g, 0.75 mmol), dibenzoyl peroxide (0.20 g, 0.10 mmol), 2 ml, 2.5 h. PLC (25% CH_2Cl_2/C_6H_6) gave the cis/*trans* isomers (22b) in a 1:1 ratio (0.178 g, 74%); IR (film) : 1740, 1215 (lactone), 1630 (C=C); UV : 253 (ε 10400); ^{1}H NMR : *cis* isomer : 2.85 (m, $W_{h/2}$ 15 Hz, 1H), 3.17 (d, *J* 2 Hz, 3H), 1H), 4.54 (m, $W_{h/2}$ 19 Hz, 1H); *trans* isomer : 3.00 (m, $W_{h/2}$ 16 Hz, 1H), 3.09 (d, *J* 1 Hz, 3H), 4.42 (m, $W_{h/2}$ 21 Hz, 1H); *cis* : *trans* = 6 : 5; ^{13}C NMR : *cis* isomer : 24.7 (CH_2), 25.4 (CH_2), 26.0 (CH_2), 26.8 (CH_2), 30.6 (CH_2), 31.6 (CH_3), 33.6 (CH_2), 50.0 (CH), 82.1 (CH), 120.2 (C), 135.4 (C), 164.9 (C); *trans* isomer : 24.4 (CH_2), 25.2 (CH_2), 25.8 (CH_2), 27.3 (CH_2), 28.8 (CH_2), 30.6 (CH_3), 35.0 (CH_2), 53.6 (CH), 80.1 (CH), 118.7 (C), 139.5 (C), 164.5 (C); Anal. Found : C,44.9; H,5.4; Calc. for $C_{12}H_{17}IO_2$: C, 45.0; H, 5.4%.

(3E) and (3Z)-Dihydro-3-(iodomethylene)-4,4,5,5-tetramethyl-2(3H)-furanone (23a) and (24). (6a) (0.280 g, 1.00 mmol), dibenzoyl peroxide (0.051 g, 0.21 mmol), 2 ml, 3 h. Radial chromatography (35% Et_2O/hexanes) gave : (i) (23a) (0.112 g, 40%); distilled 72°C (block)/0.04 mm; IR (film) 1748 (C=O), 1622 (C=C); UV : 250 (ε 9333); ^{1}H NMR : 1.29 (s, 6H), 1.32 (s, 6H), 7.72 (s, 1H); ^{13}C NMR : 21.8 (2 x CH_3), 23.5 (2 x CH_3), 47.6 (C), 87.3 (C), 90.4 (CH), 145.5 (C), 168.6 (C); MS, *m/z* 279.9965; Calc. for $C_9H_{13}IO_2$ 279.9962; (ii) (24) (0.062 g, 22%); distilled 79°C (block)/0.03 mm; IR (film) 1754 (C=O), 1621 (C=C); UV : 261 (ε 7259); ^{1}H NMR : 1.15 (s, 6H), 1.31 (s, 6H), 7.04 (s, 1H); ^{13}C NMR : 23.2 (2 x CH_3), 23.3 (2 x CH_3), 50.2 (C), 83.3 (CH), 85.6 (C), 146.3 (C), 167.7 (C); Anal. Found: C, 38.7; H, 4.7; I, 45.9; Calc. for $C_9H_{13}IO_2$ C, 38.6; H, 4.7; I, 45.3%.

(3E)-Dihydro-3-(1-iodoethylidene)-4,4,5,5-tetramethyl-2(3H)-furanone (23b). (6b) (1.400 g, 4.8 mmol), dibenzoyl peroxide (0.110 g, 0.45 mmol), 2 ml, 3.5 h. Radial chromatography (25% CH_2Cl_2/C_6H_6) gave (23b) as pale yellow crystals (1.10 g, 79%); IR (film) : 1745, 1231 (lactone), 1620 (C=C); UV : 253 (ε 7080); ^{1}H NMR : 1.23 (s, 6H); 1.29 (s, 6H); 3.25 (s, 3H); ^{13}C NMR : 22.5 (2 x CH_3), 23.3 (2 x CH_3), 34.4 (CH_3), 49.1 (C), 85.9 (C), 115.7 (C), 138.3 (C), 166.8 (C); 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%.

(3E)-Dihydro-3-(iodomethylidene)-5-phenyl-2(3H)-furanone (25a). (7a) (0.309 g, 1.03 mmol), dibenzoyl peroxide (0.058 g, 0.24 mmol), 2 ml, 24 h. Radial chromatography (40% $CHCl_3/C_6H_6$) gave (25a) as pale yellow oil (0.113 g, 37%); distilled 80°C (block)/0.04 mm; IR (film) 1759 (C=O), 1634 (C=C); UV : 212 (ε 9000), 250 (ε 8500); ^{1}H NMR : 2.79 (ddd, *J* 18, 6, 3 Hz, 1H), 3.31 (ddd, *J* 18, 8, 3 Hz, 1H), 5.59 (dd, *J* 8, 6 Hz, 1H), 7.20-7.50 (m, 5H), 7.89 (t, *J* 3 Hz, 1H); ^{13}C NMR 40.7 (CH_2), 77.2 (CH), 94.4 (CH), 125.4 (2 x CH), 128.8 (CH), 129.0 (C + 2 x CH), 139.5 (C), 165.6 (C); Anal. Found; C, 44.2; H, 2.9; I, 42.0; Calc. for $C_{11}H_9IO_2$ C, 44.0; H, 3.0; I, 42.3%.

(3E)-Dihydro-3-(1-iodoethylidene)-5-phenyl-2(3H)-furanone (25b). (7b) (0.285 g, 0.91 mmol), dibenzoyl peroxide (0.030 g, 0.12 mmol), 2 ml, 14 h. Radial chromatography (25% Et_2O/hexanes) gave (25b) as a pale yellow solid (0.219 g, 77%); mp 90°C; IR (film) : 1748, 1265 (lactone), 1644 (C=C); UV : 253 (ε 7650); ^1H NMR : 2.91 (m, $W_{h/2}$ 27 Hz, 1H), 3.16 (t, *J* 2 Hz, 3H), 3.39 (m, $W_{h/2}$ 28 Hz, 1H), 5.50 (t, *J* 8 Hz, 1H), 7.35 (m, 5H); ^{13}C NMR : 30.2 (CH_3), 45.9 (CH_2), 76.1 (CH), 119.2 (C), 125.4 (2 x CH), 128.6 (CH), 128.9 (2 x CH), 131.6 (C), 139.8 (C), 164.0 (C); MS, *m/z* : 314 (M^+); Anal. Found : C, 46.1 ; H, 3.5; I, 40.6; Calc. for $C_{12}H_{11}IO_2$: C, 45.9; H, 3.5; I, 40.4%.

(3E)-Dihydro-3-iodomethylene-5-methyl-5-phenyl-2(3H)-furanone (26). (8a) (0.103 g, 0.33 mmol), dibenzoyl peroxide (0.008 g, 0.033 mmol), 2.5 ml, 3.8 h. PLC (25% Et_2O/hexanes) gave (26) as an off-white solid (0.059 g, 57%); sublimed 100°C (block)/0.03 mm; IR (film) : 1748, 1270 (lactone), 1634 (C=C); UV : 252 (ε 8265); ^1H NMR : 1.77 (s, 3H), 3.06 (d, *J* 3 Hz, 2H), 7.39 (m, 5H), 7.86 (t, *J* 3 Hz, 1H); ^{13}C NMR : 30.7 (CH_3), 47.0 (CH_2), 83.5 (C), 94.5 (CH), 124.1 (2 x CH), 127.9 (CH), 128.8 (2 x CH), 140.3 (C), 144.4 (C), 165.0 (C); Anal. Found : C, 45.9; H, 3.3; Calc. for $C_{12}H_{11}IO_2$: C, 45.9, H, 3.5%.

(3E,3bα,8bα)-3b,b-Dihydro-3-iodomethylene-2H-indeno[1,2-b]furan-2-one (27). (9) (0.214 g, 0.69 mmol), dibenzoyl peroxide (0.030 g, 0.12 mmol), 2 ml, 5 h. PLC (25% Et_2O/hexanes) gave (27) as an oil (0.071 g, 33%); IR (film) : 3060, 1638 (C=CH), 1755, 1260 (lactone); ^1H NMR : 3.13 (dd, *J* 17, 4 Hz, 1H), 3.66 (dd, *J* 17, 10 Hz, 1H), 3.82 (m, $W_{h/2}$ 24 Hz, 1H), 5.93 (d, *J* 8 Hz, 1H), 7.34 (m, 3H), 7.54 (d, *J* 7 Hz, 1H), 7.91 (d, *J* 3 Hz, 1H); ^{13}C NMR : 37.8 (CH_2), 44.7 (CH), 84.9 (CH), 95.9 (CH), 125.2 (CH), 126.6 (CH), 127.7 (CH), 130.5 (CH), 138.4 (C), 142.5 (C), 144.2 (C), 166.3 (C); Anal. Found : C, 46.1; H, 2.9; I, 40.4; Calc. for $C_{12}H_9IO_2$: C, 46.2; H, 2.9; I, 40.7%.

(3E)-Dihydro-3-iodomethylene-2(3H)-furanone-5-spiro-1'-cyclopentane (28). (10) (0.104 g, 0.37 mmol), dibenzoyl peroxide (0.029 g, 0.12 mmol), 2.5 ml, 8.8 h. PLC (25% Et_2O/hexanes) gave (28) as a solid (0.039 g, 37%); sublimed 73°C (block)/0.02 mm; IR (film) : 3058 (C=CH); 1755, 1269 (lactone); UV : 250 (ε 11008); ^1H NMR : 2.82 (d, *J* 3 Hz, 2H), 7.77 (t, *J* 3 Hz, 1H); ^{13}C NMR : 23.6 (CH_2), 39.7 (CH_2), 42.6 (CH_2), 91.4 (C), 93.3 (CH), 141.2 (C), 165.3 (C); Anal. Found : C, 39.1; H, 3.5; Calc. for $C_9H_{11}IO_2$: C, 38.9; H, 4.0%.

(3E)-3-Iodomethylene-1-oxaspiro[4.5]decan-2-one (29). (11) (0.090 g, 0.53 mmol), dibenzoyl peroxide (0.043 g, 0.18 mmol), 1 ml, 3 h. PLC (25% Et_2O/hexanes) gave (29) (0.040 g, 45%); IR (CCl_4) 1751 (C=O); 1635 (C=C); UV : 236 (ε 9923); ^1H NMR (200 MHz) : 1.60 (m, 10H); 2.59 (d, *J* 3 Hz, 2H); 7.79 (t, *J* 3 Hz, 1H); ^{13}C NMR (50 MHz) : 22.5 (CH_2); 24.7 (CH_2); 37.8 (CH_2); 44.0 (CH_2); 83.2 (C); 94.0 (CH); 140.9 (C); 165.2 (C); Anal. Found : C, 41.2; H, 4.2; Calc. for $C_{10}H_{13}IO_2$: C, 41.1; H, 4.4%.

cis/trans-(3E)-8-t-Butyl-3-iodomethylene-1-oxaspiro[4.5]decan-2-one (30) and (31). (12) (0.31 g, 0.89 mmol), dibenzoyl peroxide (0.058 g, 0.24 mmol), 2 ml, 5 h. PLC (25% Et_2O/hexanes) gave (i) (30) (0.062 g, 20%); IR (CCl_4) : 1747 (C=O); 1635 (C=C); UV : 235 (ε 13037); ^1H NMR (200 MHz) : 0.87 (s, 9H); 1.48 (m, 9H); 2.56 (d, *J* 3 Hz, 2H); 7.79 (t, *J* 3 Hz, 1H); ^{13}C NMR (50 MHz) : 23.1 (CH_2); 27.6 (CH_3); 32.5 (C); 38.6 (CH_2); 45.2 (CH); 47.0 (CH_2); 82.4 (C); 93.9 (CH); 140.9 (C); 167.4 (C); MS : *m/z* 348.0604 (M^+); Calc. for $C_{14}H_{21}IO_2$: 348.0786; (ii) (31) (0.068 g, 22%); IR (CCl_4) : 1759 (C=O); 1639 (C=C); UV :

231 (ε 12822); ^{1}H NMR (200 MHz) : 0.89 (s, 9H); 1.08 (m, $W_{h/2}$ 15 Hz, 4H); 1.78 (m, $W_{h/2}$ 15 Hz, 5H); 2.61 (d, *J* 3 Hz, 2H); 7.80 (t, *J* 3 Hz, 1H); ^{13}C NMR (50 MHz) : 24.1 (CH_2); 27.6 (CH_3); 32.3 (C); 37.7 (CH_2); 41.9 (CH); 46.7 (CH_2); 83.9 (C); 94.1 (CH); 140.8 (C); 165.2 (C); MS : *m/z* 348.0604 (M^+); Calc. for $C_{14}H_{21}IO_2$: 348.0786.

cis and trans-(3'E)-Spiro[(5α-cholestane)-3,5'-(2'-oxo-3'-iodomethylenetetrahydrofuran)] (32) and (33). (13) (0.590 g, 1.0 mmol), dibenzoyl peroxide (0.080 g, 0.3 mmol), 3 ml, 4.2 h. PLC (25% Et_2O/hexanes) gave (i) (32) (0.12 g, 20%); IR (CCl_4) 1747 (C=O); 1635 (C=C); ^{1}H NMR : 0.65 (s, 3H); 0.85 (s, 3H); 0.86 (d, *J* 6 Hz, 6H); 0.90 (d, *J* 6 Hz, 3H); 2.61 (d, *J* 18 Hz, 1H); 2.67 (d, *J* 18 Hz, 1H); 7.87 (t, *J* 3 Hz, 1H); ^{13}C NMR : 11.8 (CH_3); 12.1 (CH_3); 18.7 (CH_3); 21.3 (CH_2); 22.6 (CH_3); 22.9 (CH_3); 23.9 (CH_2); 24.2 (CH_2); 28.1 (CH); 28.3 (CH_2); 28.6 (CH_2); 31.9 (CH_2); 33.4 (CH_2); 35.5 (C); 35.5 (CH); 35.5 (CH_2); 35.9 (CH); 36.2 (CH_2); 39.6 (CH_2); 40.0 (CH_2); 40.1 (CH_2); 42.7 (C); 43.0 (CH_2); 43.4 (CH); 54.2 (CH); 56.4 (CH); 56.5 (CH); 84.2 (C); 94.1 (CH); 140.9 (C); 165.1 (C); MS : *m/z* 580.2764 (M^+); Calc for $C_{31}H_{49}IO_2$; 580.2566, and (ii) (33) (0.11 g, 19%); IR (CCl_4) 1712 (C=O); ^{1}H NMR : 0.64 (s, 3H); 0.80 (s, 3H); 0.86 (d, *J* 6 Hz, 6H); 0.90 (d, *J* 7 Hz, 3H); 2.56 (d, *J* 3 Hz, 2H); 7.77 (t, *J* 3 Hz, 1H); ^{13}C NMR : 11.5 (CH_3); 12.1 (CH_3); 18.7 (CH_3); 21.0 (CH_2); 22.6 (CH_3); 22.9 (CH_3); 23.9 (CH_2); 24.2 (CH_2); 28.1 (CH); 28.2 (CH_2); 28.3 (CH_2); 31.8 (CH_2); 34.2 (CH_2); 34.2 (CH); 35.2 (C); 35.5 (CH); 35.8 (CH); 36.2 (CH_2); 39.6 (CH_2); 40.0 (CH_2); 40.9 (CH_2); 41.1 (CH_2); 42.6 (C); 45.4 (CH_2); 53.8 (CH); 56.2 (CH); 56.4 (CH); 83.2 (C); 93.8 (CH); 140.9 (C); 165.3 (C); MS : *m/z* 580.2750 (M^+); Calc.for $C_{31}H_{49}IO_2$: 580.2566.

(1R-1'S,7E,3aα,3bβ,5aα,6aα,9aα,10aβ,10bα,12aβ)-Perhydro-1-(1',5'-dimethylhexyl)-10a,12a-dimethyl-7-(iodomethylene)-1H-cyclopenta[7,8]phenanthro[3,2-b]furan-8,7H-one (34).* (14) (0.142 g, 0.25 mmol), dibenzoyl peroxide (0.019 g, 0.08 mmol), 2 ml, 20 h. PLC (25% Et_2O/hexanes) gave (34) as a white solid (0.048 g, 34%); mp 130 °C; IR (nujol) 1760, 1167 (lactone), 1634 (C=C); ^{1}H NMR 0.65 (s, 3H), 0.86 (d, *J* 7 Hz, 6H), 0.87 (s, 3H), 0.90 (d, *J* 7 Hz, 3H), 3.05 (m, $W_{h/2}$ 21 Hz, 1H), 4.59 (m, $W_{h/2}$ 11 Hz, 1H), 7.58 (d, *J* 1 Hz, 1H); ^{13}C NMR; 12.1 (CH_3), 13.3 (CH_3), 18.7 (CH_3), 20.9 (CH_2), 22.6 (CH_3), 22.9 (CH_3), 23.9 (CH_2), 24.2 (CH_2), 27.6 (CH_2), 28.1 (CH), 28.2 (CH_2), 28.4 (CH_2), 31.8 (CH_2), 34.5 (C), 34.9 (CH), 35.8 (CH), 36.2 (CH_2), 39.5 (CH_2), 39.6 (CH_2), 39.9 (CH_2), 42.5 (C), 42.9 (CH), 43.7 (CH), 54.9 (CH), 56.3 (CH), 56.4 (CH), 76.9 (CH), 90.9 (CH), 146.4 (C), 166.4 (C); MS : *m/z* 566.2615 (M^+); Calc.for $C_{30}H_{47}IO_2$: 566.2622.

(3Z,3aα,7aα)- and (3E,3aα,7aα)-Octahydro-3-(iodomethylene)-benzofuran (37) and (38). (36) (0.100 g, 0.38 mmol), dibenzoyl peroxide (0.024 g, 0.10 mmol), (1 ml), 6 h. PLC (25% $CHCl_3/C_6H_6$) gave : (i) At high R_f, unchanged (36) (0.010 g, 10%); (ii) At lower R_f, (*E*)-isomer (38) as an oil (0.020 g, 20%); distilled 90°C (block)/0.07 mm; IR (film) : 1641 (C=C), 1052 (C-O); ^{1}H NMR : 2.61 (m, $W_{h/2}$ 18 Hz, 1H), 4.09 (m, $W_{h/2}$ 9 Hz, 1H), 4.17 (dd, *J* 14, 3 Hz, 1H), 4.39 (ddd, *J* 14, 3, 1 Hz, 1H), 5.90 (m, $W_{h/2}$ 7 Hz, 1H); ^{13}C NMR : 20.9 (CH_2), 23.3 (CH_2), 27.3 (CH_2), 27.8 (CH_2), 46.4 (CH), 66.2 (CH), 74.5 (CH_2), 79.2 (CH), 156.3 (C); Anal. Found C, 40.8; H, 4.7; I, 47.6; Calc. for $C_9H_{13}IO$: C, 40.9; H, 5.0; I, 48.0%; (iii) At lowest R_f, (*Z*)-isomer (37) as an oil (0.008 g, 8%); distilled 90°C (block)/0.07 mm; IR (film) : 1642 (C=C), 1052 (C-O); ^{1}H NMR : 2.62 (m, $W_{h/2}$ 18 Hz, 1H), 3.95 (m, $W_{h/2}$ 8 Hz, 1H), 4.25 (br d, *J* 14 Hz, 1H), 4.51 (br d, *J* 14 Hz, 1H), 5.79 (br s, 1H); ^{13}C NMR : 20.3 (CH_2), 24.0 (CH_2), 24.4 (CH_2), 27.6 (CH_2), 47.5 (CH), 64.7 (CH), 70.5 (CH_2), 77.0 (CH), 157.2 (C); MS *m/z* 264.0008; Calc. for $C_9H_{13}IO$: 264.0011.

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