

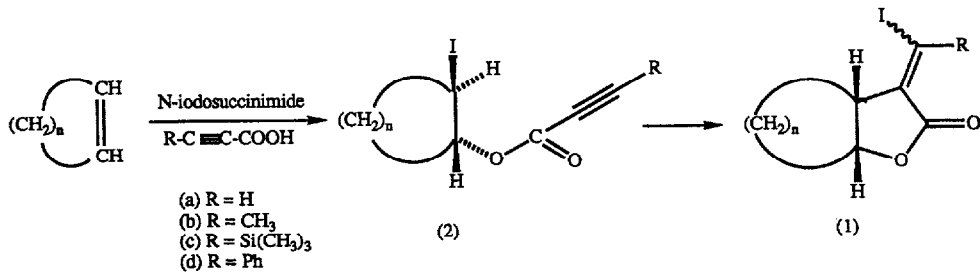
DE-IODINATION AND ISOMERISATION OF IODOALKYLIDENE LACTONES

Gerald Haaima, Anne Routledge and Rex T. Weavers*

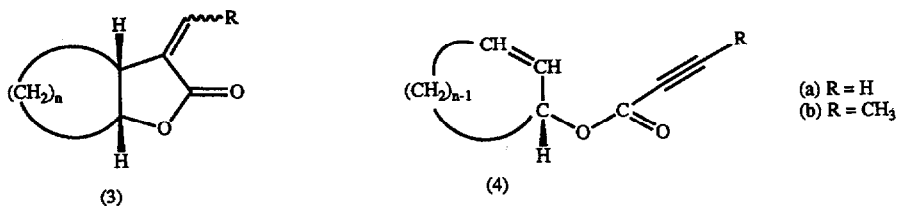
Department of Chemistry
 University of Otago
 Box 56
 Dunedin
 NEW ZEALAND.

Abstract: The (*E*)-iodoalkylidene lactones which can be formed by reaction of an alkene with *N*-iodosuccinimide and an acetylenic acid with subsequent free-radical cyclisation, are readily transformed into iodine free alkylidene lactones by photolysis. Under different reaction conditions, the photolyses yield mixtures of (*E*) and (*Z*)-iodovinylidene lactones.

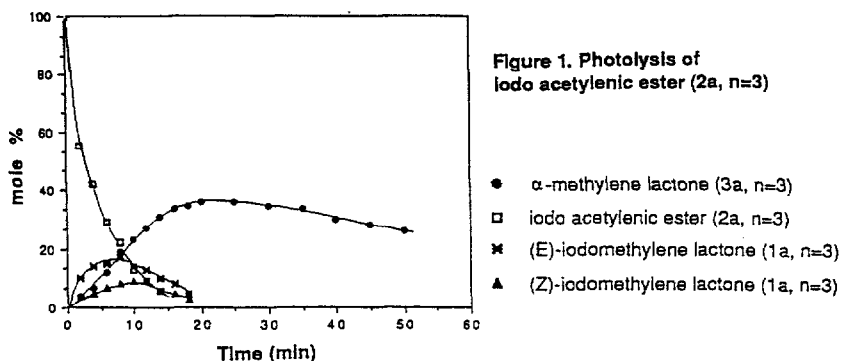
In a recent communication¹, we reported the conversion of some simple alkenes into iodoalkylidene lactones (1) via the iodo acetylenic esters (2).



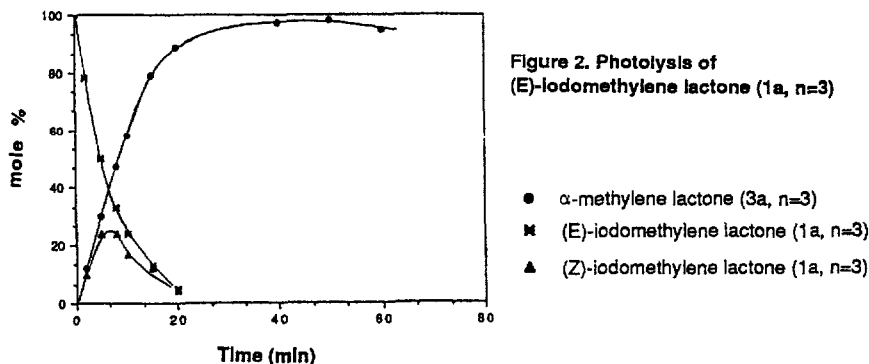
Conversion of (2) into (1) was achieved either by photolysis in the presence of zinc dust, or by heating in the presence of dibenzoyl peroxide. The latter method was superior to the former in that it gave solely the (*E*)-isomer of (1) except in the case of the phenyl derivative (1d, n=4). Photolysis produced both geometric isomers as well as small quantities of the iodine free alkylidene lactone (3). In the absence of zinc dust, the major photolysis product was the unsaturated ester (4).



The production of (3) during the photochemical synthesis of (1) suggested that it might be possible to adapt the synthesis to produce the iodine-free lactones specifically. However, when the photolyses were conducted in the presence of hydrogen atom transfer agents such as cumene, no increase in the ratio of (3) to (1) was observed. When the photolysis was monitored by gas chromatography, it became apparent that the production of (3) proceeded by initial formation of the (*E*) and (*Z*)-iodoalkylidene species (1) and that the iodine atom transfer process was not suppressed by provision of a competing hydrogen atom transfer agent. Figure 1 illustrates a typical photolysis experiment which was analysed by gas chromatography. By conducting the experiment for an appropriate length of time, yields of (3) of up to 50% could be obtained.



Photolysis of the iodoalkylidene lactones (1) was next investigated, as these were clearly implicated as intermediates in the production of the iodine-free species (3). In this case, the reaction was conducted in the absence of zinc. Figure 2 shows the progress of a typical experiment conducted on the (*E*)-iodomethylene lactone (1a, n=3), also monitored by gas chromatography.



The outcome was a very efficient transformation to the desired alkylidene lactones. Results are summarised in Table 1. The iodomethylidene lactones gave methylene lactones in excellent yield, while the iodoethylidene compounds were efficiently dehalogenated but gave mixtures of geometric isomers. The trimethylsilyl and phenyl derivatives (1c, n=4) and (1d, n=4) did not lose iodine but were isomerised to mixtures of the (*E*) and

(*Z*)-iodoalkylidene lactones. The reaction is readily adapted to larger scale synthesis. Slow passage of a solution of the iodo compound through a narrow quartz tube mounted in the reactor results in a smooth production of the de-iodinated compounds in one pass through the apparatus.

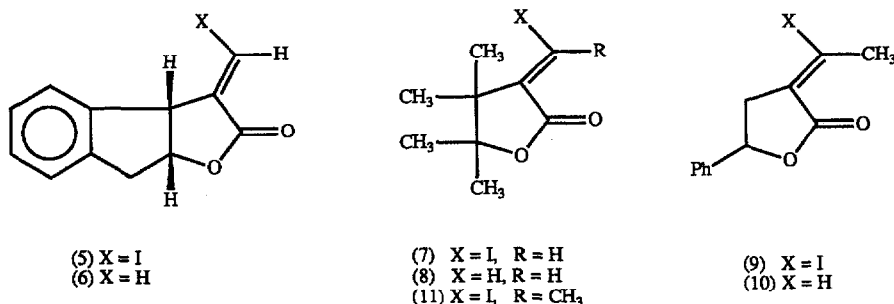


Table 1. Photodehalogenation of (*E*)-Iodovinylidene Lactones

Reactant	Product(s)	Yield ^{a,b} /(%)
1a (n=3)	3a (n=3)	98 (88)
1a (n=4)	3a (n=4)	96
1b (n=3)	3b (n=3) (<i>E:Z</i> = 1:1)	88
1b (n=4)	3b (n=4) (<i>E:Z</i> = 1:1)	84
5	6	96
7	8	94 (84)
9	10	86

a Yields calculated by g.c. for photolyses performed at 254 nm on solutions of iodo compound (0.050g) in tetrahydrofuran (20 ml) in a 10 mm i.d. quartz tube in a Rayonet photochemical reactor for 30 min.

b Isolated yields in parentheses. Reactions were conducted by passing solutions (0.008-0.009 mol dm⁻³) of the iodo compound in tetrahydrofuran through a quartz tube (length 335 mm, i.d. 2 mm) mounted in a Rayonet photochemical reactor. The flow rate was 0.25 ml min⁻¹. Purification was by preparative layer chromatography on silica (chloroform/benzene 3:7).

Figure 1 suggests that photolysis for shorter periods may be used to achieve photoisomerisation and hence to provide an alternative route to the (*Z*)-iodoalkylidene lactones which had previously been obtained in low yield from the photocyclisations of the iodo acetylenic esters. In practice it proved convenient to carry out these conversions at higher concentration in acetonitrile as solvent. Under these conditions it took approximately 30 min to achieve photo-equilibrium in most cases. Results of some isomerisations are summarised in Table 2.

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

Reactant	Time ^a /min	<i>E/Z</i> Ratio ^b
1a (n=4)	30	1:1
1b (n=3)	30	1:1
1b (n=4)	15	1:1
1c (n=4)	30	1:1
1c (n=3)	30	1:1
11	30	2.2:1

a Photolyses conducted at 254 nm on solutions of the iodoalkylidene lactone (0.25 mmol) in acetonitrile (8.5ml) in a quartz tube (8 mm i.d.) in a Rayonet photochemical reactor.

b Ratios were determined by integration of the ¹H n.m.r. spectrum.

The photochemical transformations discussed here have extended the scope of our synthetic scheme to provide a route to both geometric isomers of the iodoalkylidene lactones (1) and to the iodine-free alkylidene lactones (3).

References and Notes

1. G. Haaima and R.T. Weavers, *Tetrahedron Lett.*, **29**, 1085 (1988).
2. All new products gave satisfactory microanalytical or high resolution mass spectral data. (*E*) and (*Z*) isomers were readily distinguished on the basis of their ¹H n.m.r. resonances; protons lying close to the carbonyl group in the plane of the unsaturated system were significantly deshielded.

Acknowledgements

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