Studies on the Syntheses of Heterocyclic Compounds. Part 855.†
Cycloaddition Reaction of Bis(trimethylsilyl) Allenedicarboxylate with Homocyclic Dienes

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Halogenolactonisation of the Diels–Alder adduct (4a) derived from bis(trimethylsilyl) allenedicarboxylate (3) and furan, followed by treatment of the products (5) and (8) with diazomethane, afforded the corresponding αβ-unsaturated methyl esters (6) and (9) respectively. Catalytic hydrogenation of both compounds provided the desired methyl esters (7) and (10) which were identical to the compounds derived by Arndt–Eistert reaction of the halogenolactonic acids (11) and (13) respectively.

IN our studies towards the total synthesis of the *Rauwolfia* alkaloids, reserpine [1] (1) and its analogues, the lactonic ester (2) is essential for construction of the non-tryptamine part of these alkaloids. We have therefore examined the regioselectivity in the cycloaddition reaction of bis(trimethylsilyl) allenedicarboxylate (3)

Having thus developed a synthetic route to the important intermediate (4a), its conversion into the lactonic esters (7) and (10) was then examined.

Halogenolactonisation [3] of the cycloadduct (4a) afforded the iodolactonic acid (5) which was treated with an excess of diazomethane to give the corresponding


(1)

(2)
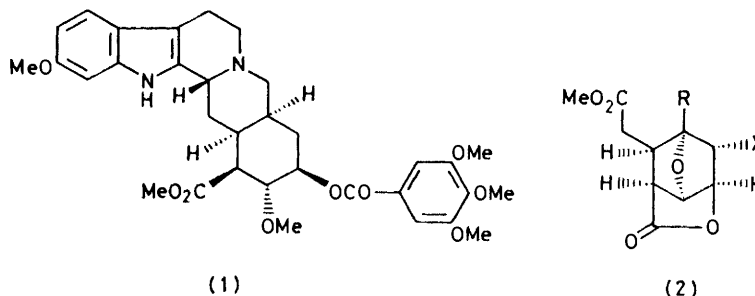
with furan and its derivatives,[2,‡] and the halogenolactonisation of the resulting cycloadduct as a preliminary experiment for an approach to (2). We now describe the results of this study.

The reactions of the allenedicarboxylate with several homocyclic dienes are summarised in the Table. All these reactions were carried out in dry benzene solution in a sealed tube. The crude reaction mixtures were treated with water in order to produce the corresponding dicarboxylic acids. The regiochemistry of the cyclo-adducts was determined by 100-MHz n.m.r. spectro-metry. In the n.m.r. spectrum of the cycloadduct (4a) derived from furan and allenedicarboxylate (3), the methine proton adjacent to the carboxy-group appeared as a double doublet at δ 3.97 with *J* values of 5 and 2 Hz. The corresponding protons in the cycloadducts (4b) and (4c) were observed as doublets (*J* 2 Hz) at δ 3.95 and 4.20 respectively, thus demonstrating that the regio-chemistry of the cycloaddition products is as represented in formula (4). This regioselectivity is rationalised by assuming that the reactants approach one another in the least sterically hindered manner as depicted in (A).

Reaction of the allene with furan derivatives

(3)   (4)
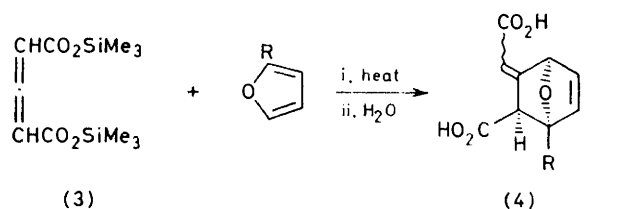
a; R = H
b; R = CH₂OCH₂Ph
c; R = CH₂OH

Diene	Reaction conditions $T/°C$	t/h	Product [a]	Yield [b] (%)
Furan	110	3.5	(4a)	88
Benzyl furfuryl ether	110	3	(4b)	8.1
	50	3	(4b)	40.4
	50	24	(4b)	52.1
Furfuryl alcohol	45	24	(4c)	23.4
	50	50	(4c)	54.8

[a] Since the dimethyl esters of these cycloadducts consisted of two compounds in the ratio of *ca.* 95 : 5, it seems that the cycloadducts (4) were mixture of double-bond geometric isomers. Further investigation of this mixture was not undertaken. [b] The yields of these cycloadducts are based on the yields of the corresponding dicarboxylic acids isolated after aqueous hydrolysis.

methyl ester (6) in almost quantitative yield. The i.r. spectrum of (6) showed carbonyl absorption bands due to the γ-butyrolactone at 1 795 cm^{-1} and to the $\alpha\beta$-unsaturated methyl ester at 1 715 cm^{-1}.

(A)
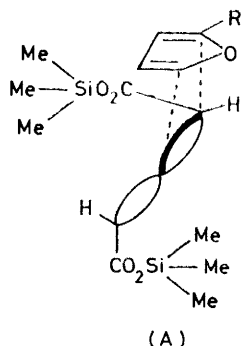
Catalytic hydrogenation of the $\alpha\beta$-unsaturated ester (6) in methanol over Adams catalyst produced the desired methyl ester (7) by selective reduction from the less hindered α-side. That this derivative (7) had the correct stereochemistry was demonstrated by comparison with an authentic sample prepared from the lactonic acid (11) by Arndt–Eistert reaction.
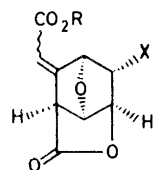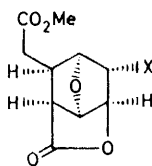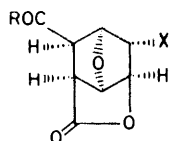

(5) R = H, X = I
(6) R = Me, X = I
(8) R = H, X = Br
(9) R = Me, X = Br
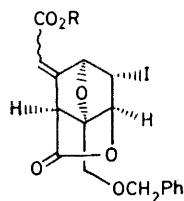
(7) X = I
(10) X = Br

(11) R = OH, X = I
(12) R = OMe, X = I
(13) R = OH, X = Br
(14) R = Cl, X = I
(15) R = CHN$_2$, X = I
(16) R = Cl, X = Br
(17) R = CHN$_2$, X = Br

(18) R = H
(19) R = Me

Thus, Diels–Alder reaction of furan with maleic anhydride in water followed by iodolactonisation without isolation of the cycloadduct according to the method of Berson et al.,[4] afforded the iodolactonic acid (11) which was also characterised as the methyl ester (12). Reaction of the lactonic acid (11) with oxalyl chloride [5] in refluxing dry benzene gave the acid chloride (14), which on treatment with an excess of diazomethane in ether provided the diazoketone (15) in 80% yield from the lactonic acid. The i.r. spectrum of this compound showed an absorption band due to the diazo-group at

2 150 cm^{-1} and a carbonyl absorption band due to the γ-butyrolactone at 1 790 cm^{-1}. This diazoketone was refluxed in absolute methanol in the presence of freshly prepared silver oxide for 1 h to afford the desired methyl ester (7). The t.l.c. behaviour and i.r. and n.m.r. spectra of this ester were identical to those of the compound (7) derived from the allenedicarboxylate and furan.

The bromolactonic ester (10) was also prepared, by the method described above, from the dicarboxylic acid (4a) via the bromolactonic acid (8). The ester was identical (t.l.c. behaviour and i.r. and n.m.r. spectra) to an authentic sample of (10) prepared from the known bromolactonic acid (13) [4] via the acid chloride (16) and the diazoketone (17).

Halogenolactonisation of the dicarboxylic acid (4b) was also examined in order to confirm its stereochemistry. Iodolactonisation of the dicarboxylic acid gave the expected iodolactonic acid (18) in high yield, which was also characterised as the corresponding methyl ester (19). This indicated the relative configuration between the carboxy-group and the ether bond in the starting dicarboxylic acid (4b) to be cis.

EXPERIMENTAL

M.p.s were determined on a Yazawa micro-apparatus. I.r. spectra were recorded with a Shimazu IR-400 spectrophotometer. Mass spectra were obtained with Hitachi M-52G and JEOL-MJS-OISG-E spectrometers. N.m.r. spectra were recorded for solutions in carbon tetrachloride, deuteriochloroform, or deuteriomethanol (tetramethylsilane as internal standard) with JEOL JNM-PMX-60 or JEOL JNM-PS-100 instruments.

Bis(trimethylsilyl) Allenedicarboxylate (3).—To allenedicarboxylic acid (4.4 g) at −40 °C was added during 10 min with stirring a mixture of trimethylchlorosilane (3.92 g) and hexamethyldisilazane (2.91 g) and stirring was continued for an additional 15 min. The mixture was then allowed to warm to room temperature over 30 min. Dry pentane (20 ml) was added and stirring was continued for 1 h. The precipitate of ammonium chloride was removed by filtration and washed with dry pentane. The combined filtrate and washings were evaporated, and distillation of the residue afforded bis(trimethylsilyl) allenedicarboxylate as an oil (6 g, 63.2%), b.p. 84 °C at 0.03 mmHg, δ(CCl$_4$) 0.03 (18 H, s, 6 × CH$_3$) and 5.83 (2 H, s).

Diels–Alder Reaction of Bis(trimethylsilyl) Allenedicarboxylate (3) *with Furan.*—A mixture of bis(trimethylsilyl) allenedicarboxylate (297 mg), furan (297 mg), and a catalytic amount of hydroquinone (10 mg) in dry benzene (3 ml) was heated with stirring in a sealed tube for 3.5 h at 110 °C. Evaporation afforded a pale yellow syrup. A small amount of water was added and the mixture was stirred for 5 min and then evaporated *in vacuo* to afford a solid which was washed with ether. Filtration followed by recrystallisation from methanol–water gave 6-*carboxy-methylene-2,5-epoxycyclohex-3-ene-1-carboxylic acid* (4a) (124 mg, 88%), m.p. 266—268 °C (Found: C, 54.8; H, 3.9. C$_9$H$_8$O$_5$ requires C, 55.1; H, 4.1%), $\nu_{max.}$ (KBr) 1 680 and 1 700 cm^{-1}, δ(CDCl$_3$ + CD$_3$OD) 3.97 (1 H, dd, J 5 and 2 Hz, 3-H), 5.20 (1 H, s, 1-H), 5.30 (1 H, d, J 5 Hz, 4-H), 6.0

(1 H, d, J 2 Hz, $>$C=CHCO_2H), and 6.53 (2 H, s, 5- and 6-H), m/e 196 (M^+).

This compound was also characterised as the dimethyl ester prepared by treatment with an excess of diazomethane, $\nu_{max.}$ (CHCl$_3$) 1 720 and 1 700 cm^{-1}, δ(CDCl$_3$) 3.63 (6 H, s, 2 × OCH$_3$), 3.93 (1 H, dd, J 7 and 2 Hz, 3-H), 5.17br (2 H, s, 1- and 4-H), 5.93 (1 H, d, J 2 Hz, $>$C=CHCO$_2$CH$_3$), and 6.27 and 6.43 (2 H, each dd, J 5 and 1.5 Hz), m/e 224 (M^+).

Diels–Alder Reaction of Bis(trimethylsilyl) Allenedicarboxylate (3) *with Benzyl Furfuryl Ether.*—A mixture of bis(trimethylsilyl) allenedicarboxylate (100 mg), benzyl furfuryl ether (138 mg), and a catalytic amount of hydroquinone (10 mg) in dry benzene (3 ml) was heated with stirring in a sealed tube for 24 h at 50 °C. Removal of solvent left a pale yellow syrup. A small amount of water was added to the residue and the mixture was stirred for 5 min and then evaporated *in vacuo* to give a solid which was washed with ether to afford the practically pure dicarboxylic acid (4b) (60.5 mg, 52.1%), m.p. 183—184°, $\nu_{max.}$ (KBr) 1 690 and 1 710 cm^{-1}, δ(CDCl$_3$ + CD$_3$OD) 3.95 (1 H, d, J 2 Hz, 2-H), 4.02 and 4.18 (2 H, each d, J 12 Hz, CH$_2$O), 4.68 (2 H, s, OCH$_2$Ar), 5.27 (1 H, d, J 2 Hz, 4-H), 6.01 (1 H, d, J 2 Hz, $>$C=CHCO$_2$H), 6.34 (1 H, d, J 6 Hz, 5-H), 6.51 (1 H, dd, J 6 and 2 Hz, 6-H), and 7.32 (5 H, s, ArH).

This compound was also characterised as its dimethyl ether, prepared by treatment with excess of diazomethane, $\nu_{max.}$ (CHCl$_3$) 1 720 and 1 705 cm^{-1}, δ(CDCl$_3$) 3.60 (3 H, s, OCH$_3$), 3.63 (3 H, s, OCH$_3$), 3.90 (1 H, d, J 2 Hz, 2-H), 3.97 (2 H, s, CH$_2$O), 4.60 (2 H, s, OCH$_2$Ar), 5.13 (1 H, d, J 2 Hz, 4-H), 5.90 (1 H, d, J 2 Hz, $>$C=CHCO$_2$CH$_3$), 6.20 (1 H, d, J 6 Hz, 6-H), 6.42 (1 H, dd, J 6 and 2 Hz, 5-H) and 7.24 (5 H, s, ArH), m/e 344 (M^+).

Diels–Alder Reaction of Bis(trimethylsilyl) Allenedicarboxylate (3) *with Furfuryl Alcohol.*—A mixture of bis(trimethylsilyl) allenedicarboxylate (223 mg), furfuryl alcohol (161 mg), and a catalytic amount of hydroquinone (10 mg) in dry benzene (3 ml) was heated with stirring in a sealed tube for 50 h at 50 °C. Evaporation left a yellow syrup, to which a small amount of water was added. The mixture was stirred for 5 min and then evaporated *in vacuo* to leave a solid which was washed with ether and recrystallised from ethyl acetate to give 6-*carboxymethylene*-2,5-*epoxy*-2-*hydroxymethylcyclohex*-3-*ene*-1-*carboxylic acid* (4c) (101 mg, 54.8%), m.p. 189—194° (decomp.) (Found: C, 50.3; H, 4.9. C$_{10}$H$_{10}$O$_6$·2/3H$_2$O requires C, 50.4; H, 4.8%). $\nu_{max.}$ (KBr) 1 700 and 1 720 cm^{-1}, δ(CDCl$_3$ + CD$_3$-OD) 4.20 (1 H, d, J 2 Hz, 2-H), 5.21 (1 H, d, J 2 Hz, 4-H), 6.01 (1 H, J 2 Hz, $>$C=CHCO$_2$H), 6.38 (1 H, d, J 6 Hz, 6-H), and 6.46 (1 H, dd, J 6 and 2 Hz, 5-H).

Iodolactonisation of Diels–Alder Adduct (4a).—A solution of iodine (93 mg) and potassium iodide (254 mg) in water (1 ml) was added to a stirred solution of the Diels–Alder adduct (4a) (60 mg) in 0.5N-sodium hydrogencarbonate (3 ml). After stirring for 3 h at room temperature in the dark, the mixture was made acidic by addition of 20% sulphuric acid solution and extracted with ether. The extract was washed with saturated sodium thiosulphate solution and brine, dried (MgSO$_4$), and then evaporated to leave a solid. After washing with ether, the resulting crystalline solid (67 mg, 68%) was recrystallised from methanol to afford 3,8-*epoxy*-4-*iodo*-7-*oxo*-6-*oxabicyclo*-[3.2.1]*oct*-2-*ylideneacetic acid* (5), m.p. 125—126° (decomp.) (Found: C, 33.5; H, 2.1. C$_9$H$_7$O$_5$I requires C, 33.6; H,

2.2%), $\nu_{max.}$ (KBr) 1 695 and 1 775 cm^{-1}, δ(CDCl$_3$ + CD$_3$OD), 4.25 (1 H, s, 4-H), 5.02 (1 H, s, C$_3$-H), 5.11 (1 H, d, J 5 Hz, 5-H), 5.44 (1 H, t, J 5 Hz, 6-H) and 6.09 (1 H, d, J 2 Hz, $>$C=CH·CO$_2$H), m/e 322 (M^+).

Methyl 3,8-*Epoxy*-4-*iodo*-7-*oxo*-6-*oxabicyclo*[3.2.1]*oct*-2-*ylacetate* (7).—The iodolactonic acid (5) (50 mg) was treated with an excess of diazomethane in ether at room temperature to afford the methyl ester (6) (52 mg, quantitative) after chromatography on silica gel, $\nu_{max.}$ (CHCl$_3$) 1 715 and 1 795 cm^{-1}, δ(CDCl$_3$) 3.86 (3 H, s, OCH$_3$), 4.05 (1 H, s, 4-H), 4.18 (1 H, dd, J 2 and 4 Hz, 1-H), 5.08 (1 H, s, 3-H), 5.25 (1 H, d, J 4 Hz, 5-H), 5.56 (1 H, t, J 4 Hz, 6-H), and 6.18 (1 H, d, J 2 Hz, $>$C=CHCO$_2$H).

A solution of this methyl ester (35 mg) in methanol (2 ml) was hydrogenated over Adams catalyst (30 mg) and the reaction mixture was filtered through a Celite pad. The filtrate was evaporated and the residue purified by preparative t.l.c. (50% ethyl acetate–hexane as eluant) to give a crystalline solid (21 mg, 58.9%), which on recrystallisation from hexane–benzene afforded the *iodolactonic ester* (7), m.p. 131—134 °C (decomp.) (Found: C, 33.3; H, 3.1. C$_{10}$H$_{11}$O$_5$I·H$_2$O requires C, 33.7; H, 3.7%), $\nu_{max.}$ 1 725 and 1 770 cm^{-1}, δ(CDCl$_3$) 3.63 (3 H, s, OCH$_3$), 3.99 (1 H, s, 4-H), 4.70 (1 H, d, J 5 Hz, 5-H), and 5.23 (1 H, t, J 5 Hz, 6-H).

Bromolactonisation of the Diels–Alder Adduct (4a) *and its Esterification.*—To a solution of the Diels–Alder adduct (4a) (100 mg) in 0.8N-sodium hydroxide solution (2 ml) was added a solution of sodium hydrogencarbonate (85.7 mg) in water (2 ml) and then bromine (15 drops). The mixture was stirred for 2 h at room temperature, acidified with concentrated hydrochloric acid, and extracted with ethyl acetate. The extract was washed with saturated sodium thiosulphate solution and brine, dried (MgSO$_4$), and then evaporated to afford the crude bromolactonic acid (8) which was esterified without further purification.

The resultant crude bromolactonic acid (8) was treated with an excess of diazomethane in ether for 3 h at room temperature. The solvent was evaporated off and the residue was subjected to chromatography on silica gel to give the methyl ester (9) (50 mg, 34%), $\nu_{max.}$ (CHCl$_3$) 1 720 and 1 795 cm^{-1}, δ(CDCl$_3$) 3.90 (3 H, s, OCH$_3$), 3.94 (1 H, s, 4-H), 4.13 (1 H, dd, J 2 and 5 Hz, 1-H), 4.99 (1 H, s, 3-H), 5.0 (1 H, d, J 5 Hz, 5-H), 5.53 (1 H, t, J 5 Hz, 6-H), and 6.10 (1 H, d, J 2 Hz, $>$C=CHCO$_2$H).

Methyl 4-*Bromo*-3,8-*epoxy*-7-*oxo*-6-*oxabicyclo*[3.2.1]*oct*-2-*ylacetate* (10).—A solution of the bromolactonic ester (9) (22 mg) in methanol (2 ml) was hydrogenated over Adams catalyst (30 mg). The reaction mixture was filtered through a Celite pad. The filtrate was evaporated to leave a residue which was purified by preparative t.l.c. (5% methanol–chloroform as eluant) to give a crystalline solid (16 mg, 72.3%), which on recrystallisation from hexane–benzene, afforded the *bromolactonic ester* (10), m.p. 140 °C (Found: C, 41.2; H, 3.6. C$_{10}$H$_{11}$O$_5$Br requires C, 41.3; H, 3.8%), $\nu_{max.}$ (CHCl$_3$) 1 725 and 1 780 cm^{-1}, δ(CDCl$_3$) 3.70 (3 H, s, OCH$_3$) 4.03 (1 H, s, 4-H), 4.93 (1 H, d, J 5 Hz, 5-H), and 5.37 (1 H, t, J 5 Hz, 6-H), m/e 290 and 292 (M^+).

3,8-*Epoxy*-4-*iodo*-7-*oxo*-6-*oxabicyclo*[3.2.1]*octane*-2-*carboxylic Acid* (11).—A mixture of maleic anhydride (15 g), furan (7.5 ml), and hydroquinone (100 mg) in water (35 ml) was stirred for 72 h at room temperature. Sodium hydrogencarbonate (11.3 g) was added in small portions over 10 min to the above mixture at 0 °C and the precipitate was removed by filtration. To the filtrate was added

sodium hydrogencarbonate (5 g) and then a solution of iodine (15 g) and potassium iodide (40 g) in water (75 ml) was added dropwise. The mixture was stirred for 1 h at room temperature. After adding a trace of sodium thiosulphate, the colourless precipitate was filtered off, washed with a small amount of cold water, and recrystallised from *methanol* to afford the *iodolactonic acid* (11) (13 g, 40.7%), m.p. 185—187 °C (Found: C, 31.0; H, 2.3. $C_8H_7O_5I$ requires C, 30.9; H, 2.3%), $\nu_{max.}$ (KBr) 1 720 and 1 770 cm^{-1}, δ(CDCl$_3$ + CD$_3$OD) 2.93 (1 H, dd, J 10 and 5 Hz, 1-H), 3.23 (1 H, dd, J 10 and 4 Hz, 2-H), 4.63 (1 H, s, 4-H), 4.83 (1 H, d, J 4 Hz, 3-H), 5.12 (1 H, d, J 5 Hz, 5-H), and 5.40 (1 H, t, J 5 Hz, 6-H).

The corresponding methyl ester (12) was prepared by treatment of the iodolactonic acid (11) with an excess of diazomethane, m.p. 167—169 °C, $\nu_{max.}$ (KBr) 1 730 and 1 785 cm^{-1}, δ(CDCl$_3$) 2.94 (1 H, dd, J 9 and 5 Hz, 1-H), 3.25 (1 H, dd, J 9 and 4 Hz, 2-H), 3.70 (3 H, s, OCH$_3$), 4.63 (1 H, s, 4-H), 4.86 (1 H, d, J 4 Hz, 3-H). 5.15 (1 H, d, J 5 Hz, 5-H), and 5.44 (1 H, t, J 5 Hz. 6-H).

The Iodolactonic Ester (7) *via the Diazoketone* (15).—To a suspension of the iodolactonic acid (11) (200 mg) in dry benzene (10 ml) at 0 °C was added dropwise oxalyl chloride (3 ml) and the mixture was then refluxed for 1 h under nitrogen. The solvent and the excess of oxalyl chloride were evaporated *in vacuo* to leave the acid chloride (14) which was treated with an excess of diazomethane in ether for 1 h. The solvent was evaporated off to leave a solid which was filtered off and washed with ether to afford the practically pure diazoketone (15) (172 mg, 80%) as a colourless crystalline solid, m.p. 147—149 °C, $\nu_{max.}$ (KBr) 1 790 and 2 150 cm^{-1}. This diazoketone was used in the following reaction without further purification.

A mixture of the diazoketone (15) (70 mg) and freshly prepared silver oxide (30 mg) in absolute methanol (6 ml) was refluxed for 1 h under nitrogen. The mixture was filtered through a Celite pad and the solid washed with methanol. The combined filtrate and washings were evaporated to leave a pale yellow syrup which was purified by preparative t.l.c. (CHCl$_3$–MeOH, 19 : 1 v/v) to afford the desired methyl ester (7) (50 mg, 59%). The t.l.c. behaviour and i.r. and n.m.r. spectra of this methyl ester were identical to those of the compound (7) derived from the reaction of allenedicarboxylate with furan.

The Bromolactonic Ester (10) *via the Diazoketone* (17).—To a suspension of the bromolactonic acid (13) (5 g) in dry benzene (130 ml) at 0 °C was added dropwise oxalyl chloride (120 ml) and the mixture was then refluxed for 2.5 h under nitrogen. The solvent and the excess of oxalyl chloride were evaporated *in vacuo* to leave the acid chloride (16) which was treated with an excess of diazomethane in ether for 1.5 h. The solvent was evaporated off to leave a solid which was washed with ether to afford the practically pure diazoketone (17) (4.94 g), m.p. 147—149°, $\nu_{max.}$ (KBr) 1 790 and 2 130 cm^{-1}. This diazoketone was used in the following reaction without further purification.

A mixture of the diazoketone (17) (70 mg) and freshly

prepared silver oxide (30 mg) in absolute methanol (6 ml) was refluxed for 1 h under nitrogen. After the usual work-up, the desired methyl ester (10) (45 mg. 47.4% overall) was obtained. The t.l.c. behaviour and i.r. and n.m.r. spectra of this methyl ester were identical to those of the compound (10) derived from the reaction of allenedicarboxylate and furan.

Iodolactonisation of the Diels–Alder Adduct (4b).—A solution of iodine (78 mg) and potassium iodide (211 mg) in water (1 ml) was added to a solution of the Diels–Alder adduct (4b) (50 mg) in 0.5N-sodium hydrogencarbonate (3 ml). After stirring for 3 h at room temperature in the dark, the mixture was made acidic by addition of 20% sulphuric acid solution and extracted with ether. The extract was washed with saturated sodium thiosulphate solution and brine, dried (MgSO$_4$), and evaporated to leave a solid which was purified by preparative t.l.c. (CHCl$_3$–MeOH, 8 : 2 v/v) to give the desired iodolactonic acid (18) (76.8 mg, 93.5%), m.p. 134—136 °C, $\nu_{max.}$ (CHCl$_3$) 1 700 and 1 800 cm^{-1}, δ(CDCl$_3$) 3.97 (2 H, s, CH$_2$O), 4.0 (1 H, d, J 2 Hz, 1-H), 4.03 (1 H, s, 4-H), 4.63 (2 H, s, OCH$_2$Ar), 4.98 and 5.0 (2 H, each s, 3- and 5-H), 6.05 (1 H, d, J 2 Hz, >C=CHCO$_2$-H), and 7.27 (5 H, s, ArH).

This iodolactonic acid (18) was also characterised as its methyl ester (19), prepared by treatment with an excess of diazomethane in ether, $\nu_{max.}$ (CHCl$_3$) 1 700 and 1 800 cm^{-1}, δ(CDCl$_3$) 3.77 (3 H, s, CCH$_3$), 3.97 (2 H, s, CH$_2$O), 4.0 (1 H, s, 4-H), 4.63 (2 H, s, OCH$_2$Ph), 4.97 and 5.0 (2 H, each s, 3- and 5-H), 6.05 (1 H, d, J 2 Hz, >C=CHCO$_2$CH$_3$), and 7.27 (5 H, s, ArH) (Found: M^+, 456.005 7. $C_{18}H_{17}IO_6$ requires M, 456.006 7).

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