

OPTICALLY ACTIVE α,β -UNSATURATED γ -LACTONES

STEREOSPECIFIC TRANSFORMATION OF ALLENE CARBOXYLIC ACIDS¹

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Abstract—Conditions of transformation of chiral allene carboxylic acids and their esters into α,β -unsaturated γ -lactones are described. It was found that in the case of 3a and 3b the lactonisation reaction was completely stereospecific. Configuration and optical purity of the title and related compounds have been established.

Determination of configuration of chiral allenes by chemical methods is based on their stereospecific synthesis from optically active substrates or their stereospecific transformation into optically active products.² At present only a few examples of stereospecific transformation of allenic systems are known.³

The purpose of our work^{4,5} was the recognition of a model of asymmetric induction in the synthesis of allene carboxylic esters by means of a reagent transferring the chirality from an asymmetric P atom and at the same time the derivation of the largest possible number of chiral compounds from these esters (1) as well as the determination of configuration of such derivatives and eventually optical purity. We have found that lactonisation of allene carboxylic acids (3) and their methyl esters (1) to α,β -unsaturated γ -lactones (2) in acid solution takes place fairly readily; this confirms earlier observations reported by Kohler,⁶ Akanes⁷ and more recently by Kresze *et al.*⁸

The first stage of our studies was the synthesis of racemic lactones.

(α). The coupling constant ³J_{HH} = 6 Hz indicates that AB protons are in *cis* position.

3-Phenyl-3-mesitylpropa-1,2-diene-1-carboxylic acid ester (3e) treated with boiling hydrochloric acid or with sulphuric acid in DME did not give the expected lactone. On the other hand it is known that a lactone is formed from 3,3-diphenylpropa-1,2-diene-1-carboxylic acid ester⁷ and for this reason our observation regarding acid 3e is of interest. From Dreiding models it can be seen that lactonisation of 3e is inhibited by the steric effect of ortho Me groups of mesityl substituent, which prevent the intramolecular attack of the nucleophile on C₃ (Fig. 1).

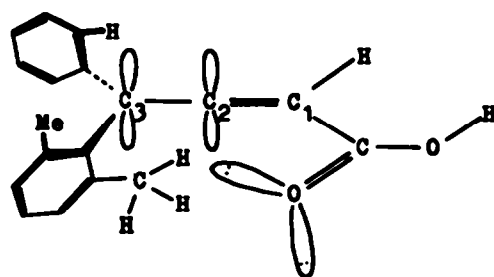
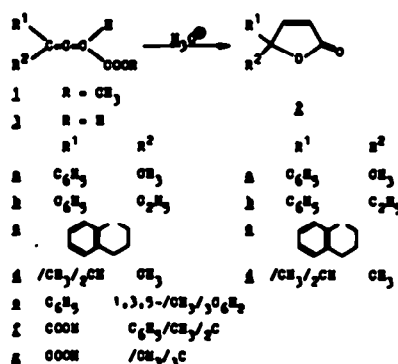


Fig. 1



Scheme 1.

We were able to carry through compounds of molecular chirality into products containing an asymmetric C atom having the structure suitable for further transformations. Fairly good yields (lower in the case of esters), stability of lactones (2) and their easy purification encouraged us to further studies on four lactones (2a, 2b, 2c and 2d). Their structure could be readily confirmed by spectroscopic methods (IR, NMR, MS). We determined the chemical shifts of the nuclei of AB system vinyl protons by introducing deuterium into the unambiguous position

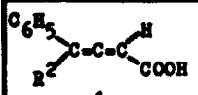
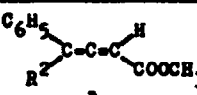
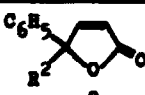
The two allene 1,3-dicarboxylic acids (3f and 3g) were also completely unreactive under the condition of the lactonisation process. One can expect this was due to the impossibility of formation of a transitional carbonium ion bearing the charge in α position to the carboxylic group.⁹

For the progress of our studies on lactones (2a, 2b and 2c) we were using optically active material in order to determine the stereospecificity of lactonisation. The methyl ester of 3,4-dimethylpenta-1,2-diene-1-carboxylic acid (1d) which was used as the substrate for 2d was available in the racemic form only. We paid attention mainly to the first two compounds (2a and 2b). The starting material consisted of optically active acids (3a and 3b) or esters (1a and 1b) of determined optical purity.⁷ The results of lactonisation are shown in Table 1.

Table 1 illustrates that the lactones obtained from the corresponding esters have a lower optical purity than those obtained from carboxylic acids under the same conditions.

The next step leading to the solution of the problem was the determination of optical purity and configuration of lactones (2a and 2b) by conversion to either atrolactic

Table 1.

 1		 3		 2			
$[\alpha]_D^{25}$ /CH ₃ OH/	e.e. %	$[\alpha]_D^{25}$ /CCl ₄ /	e.e. %	HCl-140° $[\alpha]_D^{25}$ /CCl ₄ /	H ₂ SO ₄ -DME /CCl ₄ /	e.e. %	% of racemisation
+42,53°	13,4	+41,8°	13,4	+33,35° +25,65°		12,2 9,4	9,0 30,0
-35,35°	11,1	-34,8°	11,1	-28,8° -23,3°		10,5 8,5	5,4 23,4
+43,25°	13,6	+41,7°	13,6		+37,16° +30,93°	13,6 11,3	0 17,0
-20,34°	9,13	-20,45°	9,13	-20,75° -19,40°		7,8 7,47	14,5 18,2
-20,34°	9,13	-20,45°	9,13		-23,75° -19,55°	9,13 7,52	0 17,5

n based on transformation to methyl atrolactate /Scheme 2, Table 2/

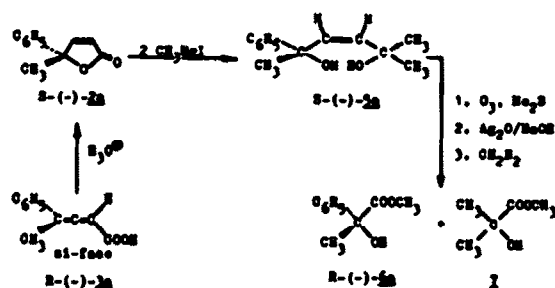
mm based on $[\alpha]_D^{25}$ of optically pure 2h confirmed by NMR spectra

acid or its methyl ester (6). For this purpose we were trying to oxidise the α,β -unsaturated (C=C) double bond using various oxidising reagents under different conditions. In spite of many attempts we were unable to obtain the completely unambiguous result, although we isolated acid MePhC (COOH)OCOCOOH (4), as directly formed by ozonolysis. Since this failure could have been due to the presence of a conjugated system we decided to eliminate it and then to oxidise the isolated double bond. For this purpose we treated (S)-(-)-2a with an excess of Grignard reagent derived from methyl iodide.

(Z)-(S)-(-)-5-Methyl-2-phenylhexen-3-diol-2,5 (5a) was formed in quantitative yield. The crude oily product (5a) was treated successively with ozone, dimethyl sulphide,¹⁰ alkaline silver oxide and finally diazomethane. The mixture of esters ((-)-6a and 7) was separated by distillation. On the basis of optical properties we reached the conclusion that the isolated levorotatory methyl atrolactate (6a)¹¹ has the (R) configuration and the same optical purity as that of substrate (R)-(-)-3a used for lactonisation. This obviously means that lactonisation of acid 3a is fully stereospecific. The results of these experiments are shown in Table 2.

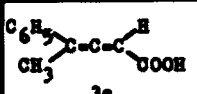
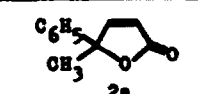
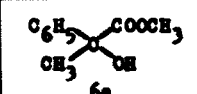
We would like to emphasise that only lactonisation of acids (3a and 3b) under mild conditions (H₂SO₄ in DME, room temp. 24 hr) gave the result confirming the complete stereospecificity. The configuration of (R)-(-)-6a was the same as that of the considered (S)-(-)-5a and the starting (S)-(-)-2a.

Obviously the intramolecular attack of the nucleophile during the lactonisation process takes place from the si face (Scheme 2) on the prochiral C atom sp² of the allene system (3a) having the (R) configuration.



Scheme 2

Table 2.

 3a		 2a		 6a	
$[\alpha]_D^{25}$ /CH ₃ OH/	e.e. %	$[\alpha]_D^{25}$ /CCl ₄ /	e.e. %	$[\alpha]_D^{25}$ /C ₂ H ₅ OH/	e.e. %
-59,5°	18,7	-51,4°	18,7	-0,94°	18,8
+42,6°	13,4	+36,5°	13,4	+0,67°	13,4

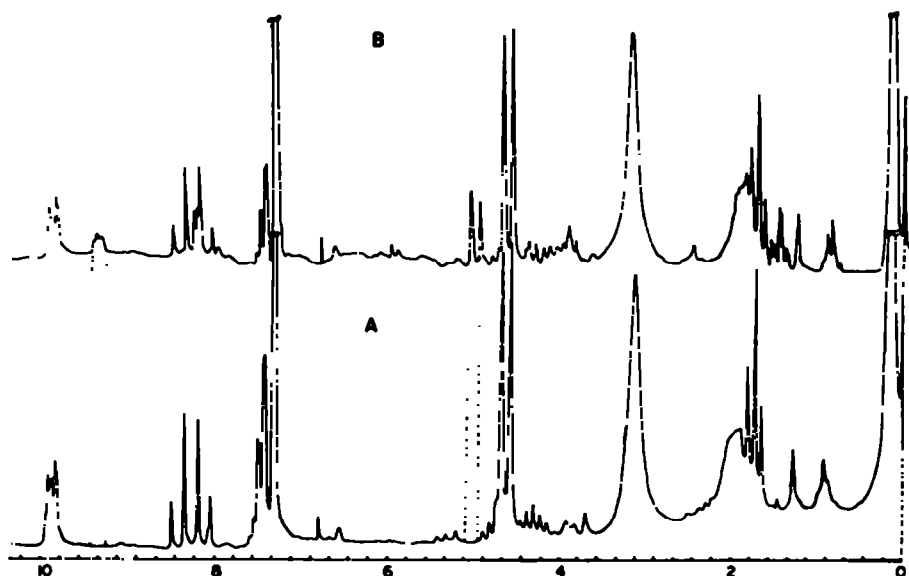


Fig. 2. ^1H NMR spectra of diol (5b) (17.3 mg) obtained from (2b) [spectrum A— $[\alpha]_D^{25} + 260^\circ$, spectrum B— $[\alpha]_D^{25} + 111^\circ$] in the presence of 89.9 mg Eu(facam) $_3$, dissolved in 0.2 ml of benzene- d_6 and 0.3 ml of carbon tetrachloride.

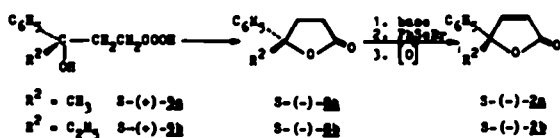
The analogous sequence of reactions carried out in the case of lactone 2b gave a positive result only in the first step. The (Z) - (S) - (-) - 2 - methyl - 5 - phenylhepten - 3 - diol - 2,5 (5b) obtained was used for another correlation.

In order to determine the configuration and optical purity of 2b and confirm our findings regarding 2a, we used the unambiguous pathway consisting in the introduction of double bond into the saturated γ -lactones (8a and 8b). For this purpose we resolved γ -hydroxy acids (9a 13,17 and 9b) which readily gave optically active γ -lactones (8a 13,17 and 8b). In the next step we used the Reich and Sharpless method for the introduction of a double bond in the α,β -position.

The configurational relationships and the optical purities of compounds (Scheme 3) are in agreement with the

results obtained for 2a on the basis of the final product of the previously described path (Scheme 2). Having obtained a sample of lactone 2b of the highest optical purity $[\alpha]_D^{25} + 260^\circ$ we examined the NMR spectrum of the degradation product of (+)-diol (5b) in the presence of Eu(facam) $_3$. We found that this sample does not give the signals of the diastereotopic Me groups in the lower field, characteristic of the (-) enantiomer. Also the signal of the nonequivalent aromatic protons (ortho) have not been detected. In the case of samples of medium purity the agreement between integrative measurements (15 experiments) in the NMR spectrum and the results of polarimetric determinations was good. In both cases (5a and 5b) the signals of diastereotopic Me groups of (+)-diol 5a and (+)-diol 5b having the configuration (R) appeared in the higher field than that of levorotatory diols (5a and 5b) which have the (S) configuration.

Lactonisation of methyl esters (1a and 1b) in acid solution gave the same results but the optical purity of the products were lower. An increase of the temperature of reaction (Scheme 1) had the same unfavourable effect (5–30% loss of optical purity).



Scheme 3

Table 3.

R^2	C_6H_5 R^2 $\text{CH}_2\text{CH}_2\text{COOH}$			C_6H_5 R^2 $\text{CH}_2\text{CH}_2\text{O}$			C_6H_5 R^2 $\text{CH}_2\text{CH}_2\text{O}$		
	$[\alpha]_D^{25}$ /C $_2$ H $_5$ OH/	o.o. %		$[\alpha]_D^{25}$ /CCl $_4$ /	o.o. %		$[\alpha]_D^{25}$ /CCl $_4$ /	o.o. %	
CH_3	2a			8a			2a		
	+5,3° -1,4°	91 24,4	S R	-66,1° +17,7°	91 24,4	S R	-248,3° +66,6°	91 24,4	S R
C_2H_5	9b			8b			2b		
	-17,4° +10,0°	100 57,5	R S	+84,7° -48,7°	100 57,5	R S	+260,4° -147,3°	100 57,5	R S

Attempted preparation of optically active spiro lactone (2c) from optically active 1c failed. The crystalline racemic lactone (2c) was exclusively formed.

We presume that lactonisation of esters (1a, 1b and 1c) takes place via hydrolysis to the corresponding acids which become cyclised to isomeric lactones (2a, 2b and 2c).

The results of our stereochemical studies could be interpreted by means of Caseiro's mechanistic suggestion³⁷ but two aspects connected with the objects of our investigation would have to be considered in such interpretation: (i) the nucleophile attacking on the electrophilic sp^2 C atom is a fragment of the molecule, (ii) the substituent (phenyl) stabilises the carbonium ion which could be formed as intermediate. In our opinion the participation of benzyl carbonium ion (10b) is less likely than the formation of bridged π or σ complex (10a) which could rationally explain the stereospecificity of lactonisation. We believe that the following observations confirm the conclusion that benzyl carbonium ion does not participate in the cyclisation: (i) after heating of lactone 2a (7.5% e.e.) with dilute hydrochloric acid for 3 hr we quantitatively recovered 2a having much lower optical purity (2.7%; 71% of racemisation). This fact can be readily explained by postulating the participation of tertiary carbonium ion according to the $A_{AC}1$ mechanism of acid hydrolysis of esters,¹² (ii) lactonisation of optically active ester (1c) under mild conditions always leads to racemic lactone (2c) which could be due to exceptional tendency of the benzyl C atom to accept full positive charge.

EXPERIMENTAL

M.p.s and b.p.s are uncorrected. M.p.s were determined on a Böchi capillary m.p. apparatus. IR spectra were recorded on a Perkin-Elmer Infracord Model 137 with NaCl optics. NMR spectra were taken on TESLA BC-487c (80 MHz) or Bruker HX 72 spectrometers using 5–10% solns with TMS as an internal standard. Chemical shifts are given in ppm. A Perkin-Elmer photopolarimeter model 141 and 241 Mc were used for the measurement of optical rotations. Products purities were determined from integrated 1H spectra and GLC analyses. Mass Spectra were obtained on a LKB GCMS 2091 with 70 eV ionisation potential.

Synthesis of (±) γ -lactones (8a¹² and 8b¹⁴), (±) γ -hydroxy acids (9a^{12,15} and 9b^{14,16}), diphenylidene¹⁴ and optical resolution of 9a^{12,17} and 9b as diastereoisomeric salts of brucine were carried out according to the general procedure described earlier.

Synthesis of (±) 2-(5H)-furanones (2a, 2b, 2c and 2d) by action of acids on the methyl esters (1a, 1b, 1c and 1d) or on the acids (3a, 3b, 3c and 3d)

General procedure. Method A. The mixture of methyl ester (1a–d) or acids (3a–d) (1 mmol) with HCl (1 ml, 17%) was refluxed for 0.5–2 hr. The organic substances were extracted with ether (4 × 5 ml). The combined ether extracts were washed successively with water, sat $NaHCO_3$ aq and water. The dried extract was concentrated under reduced pressure. Distillation of the residue in high vacuum gave pure material.

Method B. Sulphuric acid (1 mmol) was dissolved in DME (1 ml) and while maintaining a temp. of 0° was added to the ester (1a, 1b, 1c, 1d) or acid (3a, 3b, 3c, 3d) (1 mmol). The mixture was left at room temp. for 24 hr. The mixture was dissolved in ether (15 ml) and cooled in an ice-water bath, then diluted with water (10 ml). The ether layer was separated and washed with water, sat $NaHCO_3$ aq and water. The dried extract was concentrated and residue was purified by distillation *in vacuo*.

(±) 5-Methyl-3-phenyl-2-(5H)-furanone (2a). The reaction was carried out using the procedure (A) or (B) described above with 1a. (2a, 68%); b.p. 116–20° bath/0.1 mm (lit.¹² b.p. 180–186°/22 mm); NMR (CCl_4): 1.78 (s, 3H, CH_3), 5.91 (d, 1H, $J = 6.9$,

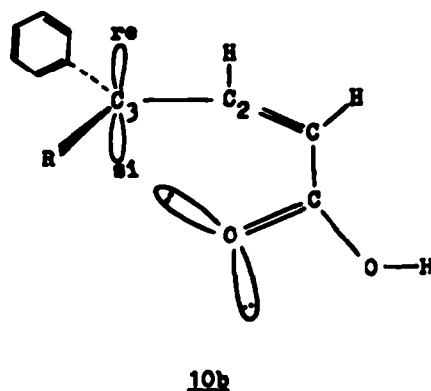
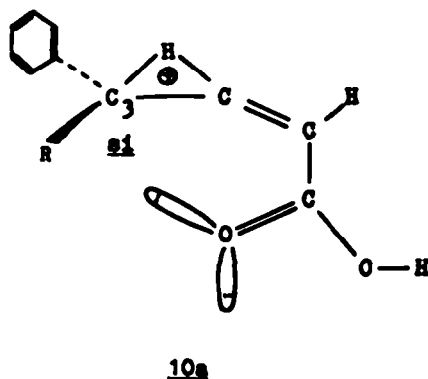


Fig. 3.

$C-C_6-H$), 7.1–7.4 (m, 5H, C_6H_5), 7.56 (d, 1H, $J = 6.9$, $H_9-C=C$); IR (film): 1770 $\nu_{C=O}$; MS: 174 (M^+) (15.5). (Found: C, 75.92; H, 5.79. Calc. for $C_{11}H_{10}O_2$: C, 75.84; H, 5.78%).

(±) 5-Ethyl-5-phenyl-2-(5H)-furanone (2b). Hydrolysis was carried out using the procedure (A) or (B) with 1b. (2b, 65%); b.p. 120–25° bath/0.1 mm; NMR (CCl_4): 0.85 (t, 3H, $J = 7.2$, CH_3), 2.04 (dq, 2H, $J = 7.2$, $-CH_2-$), 5.89 (d, 1H, $J = 5.6$, $C=C_6-H$), 7.1–7.4 (m, 5H, C_6H_5), 7.50 (d, 1H, $J = 5.6$, $H_9-C=C$); IR (film): 1770 $\nu_{C=O}$; MS: 188 (M^+) (16.6). (Found: C, 76.62; H, 6.68. Calc. for $C_{13}H_{12}O_2$: C, 76.56; H, 6.42%).

(±) 1,2,3,4-Tetrahydronaphthyl-1-spiro-5'-2,5'-H-furanone (2c). The reaction was carried out using the procedure (B) with 1c. (2c, 53%); b.p. 180–90° bath/0.4 mm; m.p. 76–7°; NMR (CCl_4): 1.9–2.1 (m, 4H, $-CH_2-CH_2-$), 2.7–3.0 (m, 2H, $-CH_2-$), 5.94 (d, 1H, $J = 5.5$, $C=C_6-H$), 6.9–7.4 (m, 4H, C_6H_5), 7.55 (d, 1H, $J = 5.5$, $H_9-C=C$); IR (film): 1770 $\nu_{C=O}$; MS: 200 (M^+) (100). (Found: C, 77.89; H, 6.19. Calc. for $C_{17}H_{14}O_2$: C, 77.79; H, 6.04%).

(±) 5-Methyl-5-isopropyl-2-(5H)-furanone (2d). The reaction was carried out using the procedure (B) with 1d. (2d, 30%); b.p. 85–90° bath/1 mm; NMR (CCl_4): 0.92 (d, 6H, $J = 6.75$ (CH_3)₂C), 1.35 (s, 3H, CH_3), 1.92 (sp. 1H, $J = 6.75$, CH), 5.94 (d, 1H, $J = 6.0$, $C=C_6-H$), 7.45 (d, 1H, $J = 6.0$, $H_9-C=C$); IR (film): 1760 $\nu_{C=O}$; (Found: C, 68.65; H, 8.39. Calc. for $C_9H_{10}O_2$: C, 68.54; H, 8.63%).

(Z)-(+)-5-Methyl-2-phenylhexen-3-diol-2,5 (3a). In a 3-neck 150 ml flask, fitted with stirrer, reflux condenser and addition funnel, was placed 480 mg (0.02 mol) of Mg turnings. Ether (20 ml) was added to cover the Mg and 2.84 g (0.02 mol) of fresh distilled MeI in ether (20 ml) was added dropwise. To this vigorously stirred mixture was added 0.87 g (0.005 mol) of 2a in ether (10 ml) at boiling while stirring for 30 min under reflux. To the cooled (–5°) mixture a soln of ammonium chloride (15 ml) was added. The layers were separated and the combined ether layers were washed with water, sat NaCl and dried. Evaporation of the solvent yielded quantitatively an oily product (3a) of satisfactory purity for further transformation. NMR ($CCl_4-C_6D_6$): 1.02 (s, 3H, $CH_3(Me)COH$), 1.14 (s, 3H, $Me(CH_2)COH$), 1.65 (s, 3H, CH_3COH), 4.90 (bs, 2H, $2 \times OH$), 5.20 (d, 1H, $J = 13$, $HC=C$), 5.57

(d, 1H, $^3J = 13$, C=CH), 7.0–7.5 (m, 5H, C_6H_5); IR (film): 3500–3000 ν_{O-H} , 1650 $\nu_{C=O}$. (Found: C, 75.17; H, 8.62. Calc. for $C_{15}H_{14}O_2$: C, 75.68; H, 8.79%).

(Z)-(+)-2-Methyl-5-phenylhept-3-diol-2,5 (5b). This material was prepared similarly to 5a. (5b) NMR (CCl_4 - C_6D_6): 0.88 (t, 3H, $^3J = 7$, CH_3 -C-COH), 1.06 (s, 3H, CH_3 (Me)COH), 1.30 (s, 3H, Me(CH₂)COH), 1.80 (q, 2H, $^3J = 7$, C-CH₂-COH), 4.0 (bs, 2H, 2 \times OH), 5.27 (d, 1H, $^3J = 13$, HC=C), 5.65 (d, 1H, $^3J = 13$, C=CH), 7.0–7.5 (m, 5H, C_6H_5); IR (film): 3500–3000 ν_{O-H} , 1660 $\nu_{C=O}$. (Found: C, 76.31; H, 9.10. Calc. for $C_{16}H_{20}O_2$: C, 76.32; H, 9.15%).

Ozonolysis of (Z)-(+)-5-methyl-2-phenylhexen-3-diol-2,5 (5a). The soln of the crude 5a (1.03 g, 5 mmol) in MeOH (30 ml) was treated with 4% O_3 at -60° . After 0.5 hr, Me_2S (2 ml) was added dropwise and the temp. increased to 20° in 3 hr. The excess of Me_2S was evaporated and to the residue was added successively MeOH (50 ml), $AgNO_3$ (1.7 g, 10 mmol in 20 ml of water) and NaOH (1.7 g in 70 ml of water) and the mixture stirred for 2 hr at 20° . The ppt was filtered off and washed with MeOH (15 ml). The filtrate was evaporated to remove MeOH. The water soln was extracted with ether. The mixture was acidified with 10% H_2SO_4 at 0° and extracted with ether (4 \times 25 ml). The solvent was evaporated and treatment of the crude acids (6a H) and (7a H) with ethereal diazomethane gave the corresponding methyl esters (6a and 7a) which were distilled *in vacuo* collecting the fraction boiling at 105–107° (0.4 mm) (lit.¹¹ 99–100°/0.1 mm) (6a, 20%). GLC indicated the ester to be pure by comparison with an authentic sample. NMR (CCl_4): 1.52 (s, 3H, CH_3 -C), 3.64 (s, 3H, CH_3 OCO), 4.0 (s, 1H, OH), 7.1–7.8 (m, 5H, C_6H_5). (Found: C, 66.40; H, 6.75. Calc. for $C_{16}H_{18}O_3$: C, 66.65; H, 6.71%). 7a was identified in GLC by comparison with an authentic sample.

(S)-(-)-5-Methyl-5-phenyl-2-(3H)-furanon (8a). The soln of (S)-(+)-9a (2 g, $[\alpha]_D^{25} + 5.3$, 91% e.e.) in dry benzene (50 ml) was gently heated in a distillation set and the solvent nearly completely removed. The operation was repeated four times. The crude product was distilled (8a, 1.65 g, 91%); b.p. 110–12° bath/0.6 mm; $[\alpha]_D^{25} - 66.1$ (c, 1.3, CCl_4); $[\alpha]_D^{25} - 52.9$, $[\alpha]_D^{25} - 55.9$ (c, 1.2, EtOH) (lit.¹² $[\alpha]_D^{25} - 54.8$ (c, 1.2, EtOH); NMR (CCl_4): 1.60 (s, 3H, CH_3), 2.20–2.50 (m, 4H, CH_2 -CH₂), 7.0–7.5 (m, 5H, C_6H_5); IR (film): 1785 $\nu_{C=O}$, 770 and 700 γ_{C-H} .

(R)-(+)-5-Ethyl-5-phenyl-2-(3H)-furanon (8b) was prepared as described above using (R)-(-)-9b (3.8 g, $[\alpha]_D^{25} - 17.4$; c, 2.5, EtOH, 100% e.e.) gave 8b (3.3 g, 96%); b.p. 110–12° bath/0.6 mm; $[\alpha]_D^{25} + 84.7^\circ$ (100% e.e.; c, 4.4, CCl_4); NMR (CCl_4): 0.82 (t, 3H, $^3J = 8$, CH_3), 2.0 (q, 2H, $^3J = 8$, Me-CH₂), 2.4 (m, 4H, -CH₂-CH₂-), ~7.3 (m, 5H, C_6H_5); IR (film): 1780 $\nu_{C=O}$.

(S)-(-)-5-Methyl-5-phenyl-2-(5H)-furanon (2a) via dehydrogenation of 8a. In a 3-neck 150 ml very dry flask, fitted with a stirrer, THF (25 ml) was placed with stirring under argon at -78° (solid CO_2 -acetone cooling bath) and ethereal soln of BuLi (22 mmol) was added dropwise so as to maintain a temp. of -70° or less, then cyclohexylisopropylamine (11 mmol) in THF (5 ml) was added at -78° . To such prepared lithium sec-amide soln 8a (1.74 g, 10 mmol) ($[\alpha]_D^{25} - 66.1$, 91% e.e.) in THF (5 ml) was added slowly at -78° and stirring was continued for 15 min. After, the THF soln of phenylselenenyl bromide (13 mmol) was added dropwise. The mixture reached gradually a higher temp., at -10° sat NH_4Cl aq was added. The organic products were extracted with ether (4 \times 10 ml) and the combined ether extracts were washed with 5% HCl, $NaHCO_3$ aq, water and dried. After

concentrating under reduced pressure, the residue was dissolved in a soln of THF (10 ml) and AcOH (15 ml). The soln was treated with 30% hydroperoxide (7 ml) at 20° and left for the night. Next, benzene (50 ml) was added and the organic layer was separated and washed with water, $NaHCO_3$ aq, water and dried. The α,β -unsaturated lactone (2a) was purified on the following way: the crude 2a was dissolved in hot 2.5 N KOH (5 ml). Then the soln was diluted with water (25 ml) and extracted with ether (3 \times 5 ml). The water layer was cooled in an ice-NaCl bath and acidified with 10% H_2SO_4 then extracted with ether (5 \times 10 ml). Ethereal soln was thoroughly washed with $NaHCO_3$ aq to remove unchanged acid (9a). The dried extracts were concentrated and the residue was distilled *in vacuo* (2a, 55%), b.p. 116–20° bath 0.1 mm, $[\alpha]_D^{25} - 248.3$ (c, 5, CCl_4), (91% e.e.).

(R)-(+)-5-Ethyl-5-phenyl-2-(5H)-furanon (2b) via dehydrogenation of 8b was prepared as described above using (R)-(+)-8b; $[\alpha]_D^{25} + 84.7^\circ$; (2b) m.p. 47–8°; $[\alpha]_D^{25} + 260.4^\circ$ (c, 5.26, CCl_4), (100% e.e.) $[\alpha]_D^{25} + 260.5^\circ$ (c, 1.1, EtOH).

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