

ASYMMETRIC PHOTOCYCLOADDITION BETWEEN FURAN AND CHIRAL ALKYL GLYOXYLATES

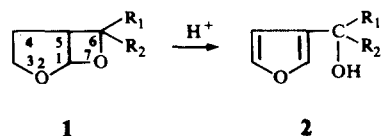
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Abstract—High-pressure mercury lamp irradiation of chiral alkyl glyoxylates [*R*(-)-menthyl, *R*(-) and *S*(+)-2-octyl, *R*(-) and *S*(+)-2, 2-dimethyl-3-butyl] with furan led to alkyl 2,7-dioxabicyclo-[3.2.0] hept-3-ene-6-carboxylates (**13a-e**) exhibiting low (2.5–7.3%) optical purity. Compounds **13a-e** were isomerized to alkyl 3-furylglycolates (**14a-e**) in good yield. Configuration *S* was assigned to levorotary methyl 3-furylmethoxyacetate. Two interpretations of the results of asymmetric synthesis were proposed.

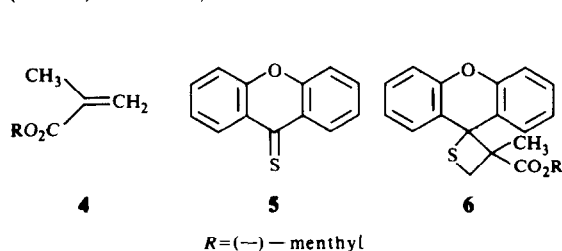
Photochemical cycloaddition of olefins to carbonyl compounds (Paterno-Buchi reaction) is one of the most convenient methods for the preparation of oxetanes.¹ When furan is employed as the olefinic component this reaction affords 6-substituted 2,7-dioxabicyclo-[3.2.0] hept-3-enes (**1**).^{1,2} It has been shown that compounds **1** can be readily isomerized to 3-furylmethanols **2**.³ This reaction represents a simple route to 3-substituted furans; many compounds of this type occur in nature.⁴



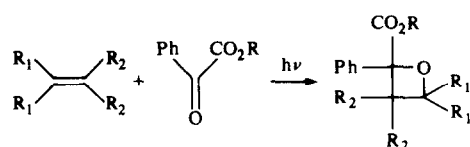
Alcohols **2** possessing a centre of chirality (when $R_1 \neq R_2$) adjacent to the furan moiety, can be prepared in optically active form either by resolution of a racemate, or by asymmetric synthesis. The latter route would involve asymmetric preparation of **1** followed by the isomerization of the photoadduct to **2**.

Photochemical asymmetric synthesis is relatively little explored. There are only few reports in the literature related to our problem.^{5,6}

Photochemical cycloaddition between *R*(-)-menthyl methacrylate **4** and xanthione **5** gave a thietane **6**. The optical purity of **6** was dependent on the wavelength of the light used; it amounted to 17% when **4** reacted in the T_1 state ($n \rightarrow \pi^*$, $\lambda = 589$ nm), and only 6% for the S_2 state ($\pi \rightarrow \pi^*$, $\lambda = 400$ nm).⁵



Gotthardt and Lenz reported that irradiation of *R*(-)-menthyl phenylglyoxylate **7** in the presence of olefin **8** or **9** afforded chiral oxetanes **10** and **11**, respectively, of relatively high optical purities: 53 and 37%.⁶



- 8** $R_1 = R_2 = \text{CH}_3$ **7** **10** $R_1 = R_2 = \text{CH}_3$
9 $R_1 = \text{H}, R_2 = \text{OCH}_3$ $R = (-)$ -menthyl **11** $R_1 = \text{H}, R_2 = \text{OCH}_3$

Photochemical asymmetric synthesis of **1** appeared to us—in light of the above results—interesting and worth of study. We have chosen optically active alkyl glyoxylates **12'** as components of the reacting system (Scheme 1).

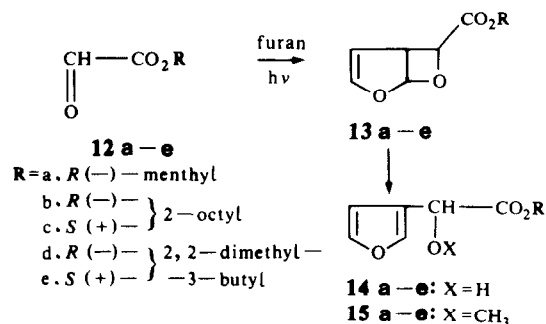
Photocycloaddition between furan and aldehydes is remarkably regio- and stereospecific: it affords exclusively bicyclic adducts **1** with an *exo* positioned substituent at C-6.^{1,2,8}

Irradiation of the appropriate alkyl glyoxylate **12a-e** with furan, at room temperature by a high pressure mercury lamp yielded chiral alkyl 2,7-dioxabicyclo-[3.2.0] hept-3-ene-6-carboxylates **13a-e**.

The results of photocycloaddition leading to **13** are collected in Table 1.

Isomerization of **13a-e** to alkyl 3-furylglycolates **14a-e** was readily affected by *p*-toluenesulfonic acid in ether solution. The yields and properties of esters **14a-e** are summarized in Table 2.

The main problem was now the preparation of optically pure 3-furylglycolic acid **16**. The absolute configuration of this compound is unknown. Acid **16**, obtained



Scheme 1.

Table 1. Photocycloaddition of optically active alkyl glyoxylates **12** to furan

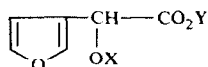
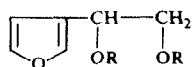
Photoadduct 13 ; Yield % R =	Yield %	[α] ₅₈₉ (c, 1.5) ^a (t°C)	b.p. ^b °C/Torr	Formula	Analysis %			
					Calc.		Found	
					C	H	C,	H
<i>R</i> (-)-menthyl 13a	80	-42.3° (20)	120/0.02	C ₁₆ H ₂₄ O ₄	68.2	8.6;	68.5	8.7
<i>R</i> (-)-2-octyl 13b	71	-11.2° (19)	120/0.2	C ₁₄ H ₂₂ O ₄	66.1	8.7;	66.3	9.1
<i>S</i> (+)-2-octyl 13c	70	+11.0° (20)	120/0.2					
<i>R</i> (-)-2,2-dimethyl-3-butyl 13e	67	-5.1° (17)	100/0.4	C ₁₂ H ₁₈ O ₄	63.7	8.0;	63.3	8.3
<i>S</i> (+)-2,2-dimethyl-3-butyl 13e	66	+5.3° (17)	100/0.4					

^ain ethanol; ^bair-bath temperatureTable 2. Isomerization of photoadducts **13** to alkyl 3-furylglycolates **14a-e**

Ester 14 ; R =	Yield %	[α] ₅₈₉ (c, 1.5) ^a (t°C)	b.p. ^b °C/Torr	Formula	Analysis %			
					Calc.		Found	
					C,	H	C,	H
<i>R</i> (-)-menthyl 14a	70	-61.4° (18)	120/10 ⁻⁴	C ₁₆ H ₂₄ O ₄	68.5	8.6;	68.5	8.8
<i>R</i> (-)-2-octyl 14b	75	-10.2° (19)	100/10 ⁻³	C ₁₄ H ₂₂ O ₄	66.1	8.7;	65.9	8.9
<i>S</i> (+)-2-octyl 14c	74	+10.1° (20)	100/10 ⁻³					
<i>R</i> (-)-2,2-dimethyl-3-butyl 14d	75	-22.8° (20)	120/0.5	C ₁₂ H ₁₈ O ₄	63.7	8.0;	63.5	8.0
<i>S</i> (+)-2,2-dimethyl-3-butyl 14e	77	+23.0° (21)	120/0.5					

^ain chloroform; ^bair-bath temperature.

after hydrolysis of the ester, **14f** is readily soluble in water. After etherification of the hydroxyl group in **14f** and hydrolysis of the ester grouping, it was possible to isolate 3-furylmethoxyacetic acid **17** in 75% yield.

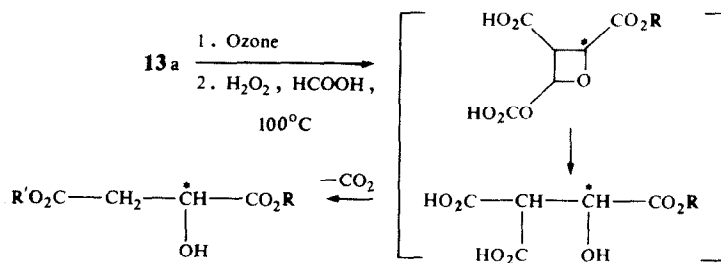
**14f**: X=H, Y=n-Bu**16**: X=Y=H**17**: X=CH₃, Y=H**18**: X=CH₃, Y=n-Bu**19**: X=Y=CH₃**20**: X=H, Y=CH₃**21**: X=ω-(—)-camphanyl, Y=CH₃**22**: R=H**23**: R R' =

This acid was resolved into enantiomers by crystallization of its brucine salt. The optical purity of the resolved acid was determined using NMR methods.⁹

Dextrorotatory 3-furylmethoxyacetic acid **17** was converted into methyl ester **19** ([α] +85.1°, CHCl₃).

Transesterification of butyl 2,7-dioxabicyclo-[3.2.0]hept-3-ene-6-carboxylate **13f** (R=n-Bu) with methanol followed by isomerization with *p*-toluenesulfonic acid afforded ester **20**. Esterification of the hydroxyl group in **20** with ω-(—)camphanyl chloride¹⁰ yielded diastereoisomeric esters **21**.

Four consecutive crystallizations from ether-chloroform gave a single diastereoisomer. Reduction with lithium aluminum hydride afforded optically pure (+)-(3'-furyl)-1,2-ethanediol **22**. ([α]₅₈₉ +15.0°, EtOH),

**24**: R=R(—)-menthyl, R'=H**25**: R=R'=H**26**: R=R'=CH₃

Scheme 2.

which was converted into the isopropylidene derivative **23**³ ($[\alpha]_{589}^{+29.6^\circ}$, CHCl_3).

Determination of the absolute configuration of compounds (+)-**19** and (+)-**22** by means of their c.d. spectra failed. We decided therefore to assign their configuration on an indirect route by degradation of the photoadduct **13a** to a chiral product of known absolute configuration. Oxidative degradation of **13a** with ozone to malic acid **25** was the most obvious choice (Scheme 2).

Monoester **24** was the last product of the degradative sequence. Hydrolysis of **24** to free acid **25**, followed by esterification with diazomethane afforded the levorotatory dimethyl malate **26**¹¹ ($[\alpha]_{546} -0.72$, methanol). The absolute configuration of levorotatory dimethyl malate is *S*¹¹; hence, the configuration at C-6 of the excessive enantiomer **13a** was also *S*.

Photoadduct **13a** was converted into levorotatory 1-(3'-furyl)-1, 2-ethanediol **17** and into levorotatory methyl 3-furylmethoxyacetate **19**, which proved the *S* configuration for those derivatives. It is worth mentioning here that the absolute configuration of the isomeric levorotatory 2-substituted furans is the reverse.¹²

All photoadducts **13a-e** were isomerized with *p*-toluenesulfonic acid to esters **14a-e**, and then converted into methyl ethers **15a-e**. Hydrolysis of the ester grouping followed by esterification with diazomethane yielded optically active methyl 3-furylmethoxyacetate **19**. Configuration and optical purities of the samples of thus prepared esters were determined by comparison with optically pure model compound (+)-*R*-**19**. The results are summarized in Table 3.

The optical purity of *R*(-)-menthyl 2,7-dioxabicyclo-[3.2.0] hept-3-ene-6-carboxylate **13a** was estimated by two independent methods: by degradation to dimethyl malate (**26**, $[\alpha]_{546} -0.72$, which corresponded to 7.2% optical purity) and by transformation to methyl 3-furylmethoxyacetate (**19**, determined optical purity 7.3%).

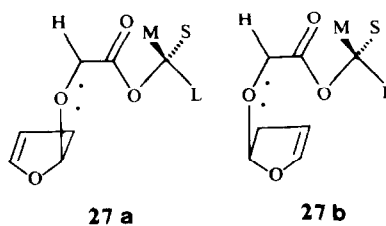
The absolute configuration of *R*-alkyl 3-furylglycolates **14** (**a,b** and **d**) was *S*; hence the configuration of photoadducts **13** (**a,b,d**) was 1*R*; 5*S*; 6*S*.

The optical purities of alkyl 3-furylglycolates **14** obtained by asymmetric synthesis were low. We examined the influence of low temperatures on the optical yield in the photochemical reaction between *R*(-)-menthyl glyoxylate **12a** and furan. However, the results achieved were not significantly different from those obtained at room temperature; at -30° enantiomeric excess corresponded to 6.5%, and at -50° to 7.1%.

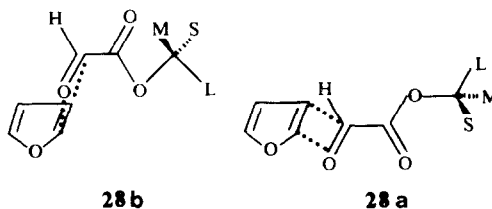
The mechanism of the photocycloaddition of carbonyl compounds to olefins is known.¹³ The reaction occurs in

two steps. In the first step a bond between oxygen atom and olefinic carbon atom is formed which leads to a diradical. Then follows the closure of the second bond. For the rationalization of the present results two hypotheses can be advanced:

(1) Photocycloaddition between furan and alkyl glyoxylate occurs in *exo* and *endo* fashion. The *exo*-type diradical **27a** forms the second bond directly, whereas in the *endo*-diradical **27b** a rotation around the C-O bond by 180° must occur before closure of the second bond. It must be remembered that the only product of the reaction is of the *exo* type.



(2) Alkyl glyoxylate enters into the *exo*-type cycloaddition with furan parallelly in two conformations: *S*-cisoid and *S*-transoid. The following transition states, **28a** and **28b**, should lead to excesses of opposite enantiomers of the bicyclic system.



The consequence of both reaction courses is the same: steric effects acting in opposite directions largely cancel inducing effects of chiral alkyl groups which results in low enantiomeric purities of products. The magnitudes of induced optical activities are not related to differences in bulkiness of substituents S-M-L around the inducing chiral centres. In view of the similarity of the present results to earlier findings achieved when optically active esters of glyoxylic acid were employed in asymmetric Diels-Alder¹¹ and ene¹⁴ syntheses we prefer the second explanation although a convincing proof for this hypothesis cannot be provided within these experiments.

Table 3. Optical purities and configuration of methyl 3-furylmethoxyacetate **19** obtained from alkyl 3-furylglycolates **14a-e**

Alkyl 3-furylglycolate 14 ; R =	Properties of ester 19		Configuration
	$[\alpha]_{546}^a$	Optical purity %	
<i>R</i> (-)-menthyl 14a	-6.24°	7.27	<i>S</i>
<i>R</i> (-)-2-octyl 14b	-4.03°	4.74	<i>S</i>
<i>S</i> (+)-2-octyl 14c	+4.13°	4.84	<i>R</i>
<i>R</i> (-)-2,2-dimethyl-3-butyl 14d	-1.94°	2.28	<i>S</i>
<i>S</i> (+)-2,2-dimethyl-3-butyl 14e	+2.07°	2.42	<i>R</i>

^a Average value obtained in two independent experiments. Rotation measurements done in chloroform solution ($c \sim 1$) at 20°C

However, photocycloaddition of furan to optically active, conformationally rigid ketones¹⁵ supplies an additional support in favor of this hypothesis.

EXPERIMENTAL

B.ps and m.ps were uncorrected. The ¹H NMR were recorded on a JEOL-JNM-4H-100 spectrometer. Rotations were measured using Perkin-Elmer PE 141 spectropolarimeter. All photochemical reactions were carried out in a Pyrex photochemical reactor,¹ using a high pressure mercury lamp (250 or 400 W), and were monitored by tlc (ligroine-ethyl acetate 7:3). Chiral alkyl glyoxylates **12a-e** were prepared according to Ref. 7.

Photochemical reaction between alkyl glyoxylate 12 and furan. Alkyl glyoxylate **12** (15 mmoles) was dissolved in 150 ml of furan and irradiated for 16-20 hr. Furan was distilled off and 50 ml of ether was added to the oily residue causing the precipitation of furan polymers. Polymers were filtered off and the filtrate was evaporated to dryness. The residue was distilled under reduced pressure yielding alkyl 2,7-dioxabicyclo-[3.2.0] hept-3-ene-6-carboxylate **13**. The results are summarized in Table 1. The ¹H NMR (CDCl₃) spectra of all photoadducts **13a-e** were almost identical, and exhibited signals characteristic for a 2,7-dioxabicyclo-[3.2.0] hept-3-ene skeleton at σ 6.65-6.75 (m, J_{3,4} = 3 Hz, H-3), 6.40-6.55 (d, J_{1,5} = 4 Hz, H-1), 5.40-5.50 (t, J_{4,5} = 3 Hz, H-4), 4.70-4.85 (d, J_{5,6} = 3.5 Hz, H-6), and 3.70 ppm (m, H-5). IR (film): 1740, 1605 cm⁻¹.

Isomerization of alkyl 2,7-dioxabicyclo-[3.2.0] hept-3-ene-6-carboxylates 13a-e to alkyl 3-furyl glycolates 14a-e. Photoadduct **13** (10 mmoles) was dissolved in 25 ml of dry ether containing 280 mg of *p*-toluenesulfonic acid monohydrate. The mixture was kept for several hours at room temperature (**13a**-16 hr; **13b** and **13c**-8 hr; **13d** and **13e**-6 hr). After neutralization with triethylamine (0.3 ml) the mixture was passed through a short column filled with neutral alumina (3g). After evaporation of the solvent crude **14** was distilled in vacuum. The results are collected in Table 2. The ¹H NMR spectra (C₆D₆) of all products **14a-e** exhibited almost identical signals (characteristic for 3-furyl-methanols) at σ 7.30-7.45 and 7.05-7.15 (both α protons of the furan moiety), 6.30-6.45 (H- β of the furan ring) 5.0-5.18 (-CH-CO₂R). Pairs of diastereoisomeric esters gave separate signals: for proton H-2 at σ 7.3-7.45 and for methine proton at δ 5.0-5.18. IR (film): 3550, 1720, 1500 and 875 cm⁻¹.

Methyl R(+)-3-furyl-methoxyacetate 19. Butyl 3-furyl glycolate³ (**14f**, 19.8 g) was dissolved in 100 ml of fresh distilled methyl iodide and 20 g of silver oxide was added. The mixture was stirred and refluxed for 12 hr. The catalyst was filtered off and the filtrate evaporated to dryness. Distillation of the crude product (110°/0.4 Torr) yielded 17.38 g (82%) of butyl 3-furyl-methoxyacetate **18**. Analysis. (Found: C, 62.0; H, 7.9. Calc. for C₁₂H₁₄O₄: C, 62.3; H, 7.6%). ¹H NMR (C₆D₆) δ 7.35, 7.04 and 6.46 (protons of the furan moiety), 4.61 (s, CH-CO₂Bu), and 3.19 (s, OCH₃). IR (film): 2980, 1510, 880 cm⁻¹.

Ester **18** (17g) was hydrolyzed with 100 ml of 10% sodium hydroxide solution for 1 hr under reflux. After cooling to room temperature the mixture was extracted with ether (to remove butanol) and acidified to pH 1 with 6N HCl. Free acid **17** was extracted five times with ether. Yield-9.38g (75%) of the crude product. An analytical sample (~0.5g) was distilled in vacuum (b.p. 105°/0.4 Torr-air bath temperature). Analysis. (Found: C, 53.5; H, 5.4. Calc. for C₇H₈O₄: C, 53.8, H, 5.2%). ¹H NMR (CCl₄) δ 7.44, 7.31 and 6.40 (protons of the furan moiety), 4.69 (s-CH-CO₂H). IR film): 3700-2700, 1740, 1510 and 875 cm⁻¹.

Acid **17** was dissolved in 20 ml of acetone and 21.15g of brucine was added. The mixture was refluxed for 10 min and left to crystallize. The precipitate (m.p. 150-157°) was crystallized four times from acetone-chloroform-acetonitrile (9:2:1) to give 2.17g of optically pure product: m.p. 117-118°, $[\alpha]_{D}^{25}$ -10.7° (c 1.3, chloroform). M.p. and rotation did not change after the next crystallization. The brucine salt was treated with 2 ml of 6N hydrochloric acid, and free acid **17** was extracted thrice with ether. Yield: 429 mg, 11%, $[\alpha]_{D}^{25}$ +64.5° (c 1.8, chloroform).

The optical purity of this acid was proved by NMR. The signal of the methine proton of racemic acid **17** in ¹H NMR spectrum

(CCl₄) was a singlet. After addition of α -D-phenylethylamine it was split into two singlets at δ 4.18 and 4.11 that could be connected with the two diastereoisomeric salts.

Disappearance of the signal at δ 4.11 from the ¹H NMR spectrum (CCl₄) of the salt of (+)-**17** and α -D-phenylethylamine proved the complete optical purity of this acid.

Crude acid (+)-**17** was converted with diazomethane into methyl ester **19**. B.p. 95°/0.6 Torr (air-bath temperature), $[\alpha]_{D}^{25}$ +69.8°, $[\alpha]_{D}^{25}$ +85.1° (c 0.9, chloroform). Analysis. (Found: C, 56.2; H-6.2. Calc. for C₈H₁₀O₄: C, 56.5; H, 5.9%). ¹H NMR (CDCl₃) δ 7.45, 7.38 and 6.44 (furan moiety), 4.76 (s, CH-CO₂Me) and 3.78 (s, CH-CO₂Me). IR (film): 3000-2840, 1760, 1510, 880 cm⁻¹.

(+)-(3-Furyl)-1R, 2-ethanediol **22**. Butyl 2,7-dioxabicyclo-[3.2.0] hept-3-ene-6-carboxylate³ (**13f**, 19.8g) was dissolved in 500 ml of anhydrous methanol, 25 g of sodium bicarbonate was added and the mixture was stirred for 1 hr at room temperature. After evaporation of methanol, 100 ml of water was added, the product was extracted thrice with ether, and dried. The residue after evaporation of the solvent was distilled; b.p. 75-76°/0.7 Torr; yield 14.2g (91%) of methyl ester **13g** (R = Me). Ester **13g** (14g) was dissolved in 250 ml of dry ether containing 500 mg of *p*-toluenesulfonic acid monohydrate and kept for 1 hr at room temperature. After neutralization with triethylamine (0.6 ml), the product was isolated by distillation; b.p. 82°/0.6 Torr. Yield: 10.5 g (75%) of methyl 3-furyl glycolate **20**. Analysis. (Found: C, 53.6; H, 5.3. Calc. for C₇H₈O₄: C, 53.8; H, 5.2%).

Compound **20** (6.5 g) was dissolved in 50 ml of dry pyridine and ω -(-)-camphanyl chloride¹⁰ (9.5 g) was added. The mixture was kept overnight at room temperature. Then it was poured into cold water and the ester was extracted with chloroform (five times). The organic layer was washed with water, 5% hydrochloric acid, 5% sodium carbonate solution and water, and dried. Evaporation of the solvent left 12g of oily residue which crystallized after addition of ether. The crude product was crystallized four times from ether-chloroform (3:1) to give 1.96 g of optically pure ester **21** (m.p. 137-8°, $[\alpha]_{D}^{25}$ +39.3°, c 1.1, chloroform). The resolution of the ester was monitored by ¹H NMR.¹⁰ The mixture of diastereoisomeric esters **21** exhibited six singlets of the camphanyl moiety in the ¹H NMR spectrum [CDCl₃; in the presence of Eu (fod)₃]. Disappearance of the three signals from the spectrum of the ester obtained after fourth crystallization proved its optical purity. Analysis. (Found: C, 61.3; H, 6.1. Calc. for C₁₇H₂₀O₇: C, 60.7; H, 6.0%). IR (KBr): 3160, 3000, 1790, 1750, 1730, 1510 and 880 cm⁻¹.

Optically pure ester **21** was reduced with 700 mg of lithium aluminum hydride in 40 ml of dry THF. The product of the reduction (isolated in usual manner) constituted a chromatographically inseparable mixture of diol **22** and camphanyl alcohol. The mixture was dissolved in 50 ml of dry acetone containing 2 drops of conc. sulfuric acid and left overnight at room temperature. Neutralization with triethylamine (5 drops) and evaporation of the solvent left an oily residue from which the *O*-isopropylidene derivative **23**³ was isolated by chromatography (benzene-ether 95:5). Yield: 350 mg, $[\alpha]_{D}^{25}$ +29.6° (c 1.5, chloroform).

Acetonide **23** (200 mg) was dissolved in 20 ml of dry methanol containing 10 mg of *p*-toluenesulfonic acid monohydrate and kept for 4 hr at room temperature. The mixture was neutralized with tri-ethylamine (2 drops) and the product was isolated by chromatography (ligroine-ethyl acetate 1:1) Yield of 1-(3'-furyl)-1,2-ethanediol³ 100 mg, m.p. 55°C, $[\alpha]_{D}^{25}$ +15.0°, $[\alpha]_{D}^{25}$ +17.9° (c 1.6, ethanol).

Ozonolytic degradation of optically active R(-)-menthyl 2,7-dioxabicyclo-[3.2.0] hept-3-ene-6-carboxylate 13a. Ozonolysis of 3.0 g of R(-)-menthyl ester **13a** in 100 ml of methylene chloride was performed at -70°. The solvent was evaporated under reduced pressure (below 25°). To the crude ozonide 15 ml of 85% formic acid and 15 ml of 30% H₂O₂ were added; the mixture was heated at 100° for 1.5 hr, whereupon H₂O₂ and HCOOH were removed under reduced pressure. The residue containing R(-)-menthyl malate was hydrolyzed with 50 ml of 6% HCl (100°, 30 min); menthol was removed by careful steam distillation. Evaporation of the solvent left crude malic acid which was dissolved in 30 ml of methanol and esterified with diazomethane.

Table 4. Alkyl 3-furylmethoxyacetates **15a-e**

Ester 15 ; R =	Yield %	b.p. ^a °C/Torr	[α] ₅₈₉ ^b (t °C)	Formula	Analysis %			
					Calc.		Found	
					C,	H	C,	H
R(-)-menthyl 15a	80	145/0.2	-69.2° (20)	C ₁₇ H ₂₆ O ₄	69.4	8.9;	69.0	9.2
R(-)-2-octyl 15b	86	110/0.4	-13.7° (20)	C ₁₅ H ₂₄ O ₄	67.1	9.0;	67.2	9.3
S(+)-2-octyl 15c	85	110/0.4	+13.7° (20)					
R(-)-2,2-dimethyl-3-butyl 15d	77	105/0.4	-27.1° (17)	C ₁₃ H ₂₀ O ₃	65.0	8.4;	64.9	8.8
S(+)-2,2-dimethyl-3-butyl 15e	75	105/0.4	+26.9° (17)					

^aAir-bath temperature, ^bin chloroform, c ~ 1

Dimethyl malate was isolated by chromatography (eluent: chloroform-acetone-ethyl acetate 2:1:1) and distilled; b.p. 125°/20 Torr (air-bath temperature) [α]₅₈₉-0.6°, [α]₅₄₆-0.72° (c 5.7, methanol). Yield: 521 mg (30.5%). IR spectrum of this compound was identical with the spectrum of the original material.

Reduction of ester 14a to diol 22. Ester **14a** (560 mg) was reduced with 70 mg of lithium aluminum hydride in 5 ml of dry ether. Product was isolated by chromatography (ligroine-ethyl acetate 3:2). Yield: 179 mg, [α]₅₈₉¹⁸-1.08° (c 3.1, ethanol).

Conversion of alkyl 3-furyl glycolates 14a-e into methyl 3-furylmethoxyacetate 19. Esters **14a-e** (6 mmoles each) were dissolved in 10 ml of methyl iodide and stirred under reflux with 1.5 g of silver oxide for 12 hr. Alkyl 3-furylmethoxyacetates **15a-e** were isolated by chromatography (ligroine-ethyl acetate 7:3). Yields, physical and analytical data are collected in Table 4. The ¹H NMR (CDCl₃) spectra of all methyl ethers **15a-e** were similar and exhibited signals at δ7.30, 7.05 and 6.50 (protons of the furan moiety), 4.60 (CH-CO₂R) and 3.20 (OCH₃).

Esters **15a-e** (3 mmoles) were hydrolyzed with 10% sodium hydroxide (10 ml) for 1 hr. Optically active alcohols (menthol, both 2-octanols or both 2,2-dimethyl-3-butanols) were removed by careful steam distillation. The product, acid **17**, was isolated by extraction with ether (after acidification to pH 1) and esterified with diazomethane to methyl 3-furylmethoxyacetate **19** (yield: 60-73%). The optical purities and configuration of this ester are shown in Table 3.

Photochemical reaction between R(-)-menthyl glyoxylate 12a and furan at low temperatures. Low-temperature photochemical reactions of **12a** and furan were carried out in a cooling thermostat (Ultra-Kryostat N-180) at -30° and -50°, using a high pressure mercury lamp (250 W) cooled with a mixture of ethanol-solid carbon dioxide. The product, R(-)-menthyl 2,7-dioxabicy-

clo-[3.2.0] hept-ene-6-carboxylate **13a** was converted into methyl 3-furylmethoxyacetate **19** in about 30% overall yield. Optical rotation of **19**: from photoadduct obtained at -30°: [α]₅₈₉²¹-4.6°, [α]₅₄₆²¹-5.6° (c 3.7, chloroform), and at -50°: [α]₅₈₉²⁰-4.8°, [α]₅₄₆²⁰-6.1° (c 3.6, chloroform).

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