A FACILE EPOXIDATION OF 5-METHYLENE-1,3-DIOXANE-4,6-DIONES WITH HYDROGEN PEROXIDE WITHOUT CATALYST

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Abstract —— 5-Methylene-1,3-dioxane-4,6-diones readily reacted with hydrogen peroxide without any catalyst and any bases to afford the spiro- and poryspirocyclic compounds containing an oxirane ring as good crystalline products. Furthermore, the epoxidation of chiral 5-arylidene-1,3-dioxane-4,6-diones with hydrogen peroxide produced the two diastereomers whose purification by silica gel chromatography ensures 100% optical purity.

INTRODUCTION

The epoxidation of α,β-unsaturated carbonyl compounds is one of very important and useful methods in organic synthesis. Several synthetic methods for the epoxidation[1] of α,β-unsaturated carbonyl compounds have been known, e.g., (i) the Weitz-Scheffer reaction,[2] (ii) the Payne method[3] and its applied synthetic methods,[2k,4] (iii) the epoxidation using peracids[5,6] or alkylhydroperoxides,[4a,7] and (iv) the epoxidation using other oxidants.[8] It has been expected that hydrogen peroxide, which is an effective oxidant for the epoxidation of the α,β-unsaturated carbonyl compounds,[1-4] has used in methods (i) and (ii) as an oxidant. Since the nucleophilicity of hydrogen peroxide is very weak by itself, in many cases, the epoxidations of mono- or disubstituted electron-deficient alkenes possessing carboxyl, alkoxycarbonyl, carbonyl, or cyano groups have required careful pH control of the reaction[2,6d,9] and/or the presence of catalysts.[3,4] However, several tri- and tetrasubstituted electron-deficient alkenes have been converted to epoxides by the reaction with hydrogen peroxide in the absence of any catalyst and no required pH control, e.g., the reaction of tetracyanoethylene with hydrogen peroxide gives tetracyanoethyleneoxide.[10]

In previous reports, 5-alkylidene-1,3-dioxane-4,6-diones, alkylidene Meldrum's acids, have acted as trapping reagents such as the dienophiles for the *o*-quinodimethanes, (*E*)-photoenols of 2-methylbenzaldehyde,[11] 2-methylacetophenone,[12] and 2-methylbenzophenone.[12] Furthermore, methylene Meldrum's acids are well-known as organic Lewis acids.[13] With such properties, these compounds are very reactive electrophiles[13-17] and are susceptible to attack by some nucleophiles such as sodium methoxide,[13] amines,[16] and aryloxide ions[17] to afford the corresponding zwitterionic adducts. Therefore, the methylene Meldrum's acids, which possess two electron-withdrawing groups, are expected to be epoxidized under milder conditions by hydrogen peroxide in the absence of any catalysts and any bases.[15] In this paper, we wish to report the facile epoxidation of the methylene Meldrum's acid with hydrogen peroxide.

RESULTS AND DISCUSSION

The treatment of isobutylidene Meldrum's acid (**1a**) with 35% hydrogen peroxide in acetonitrile at room temperature afforded an epoxide (**2a**) as colorless crystals in 76% yield. The structure of **2a** was established from a microanalysis and spectroscopic data. For example, the microanalysis showed an increase by one oxygen atom in the composition of **1a**. In the ^1H nmr spectrum of **2a**, the presence of four methyl protons and two sp^3-methine protons was revealed. In addition, in the ^{13}C nmr spectrum, signals of 2-C and 3-C of **2a** appeared at δ 75.5 and 55.4 ppm, respectively, and two carbonyl carbons were observed at different magnetic fields (δ 161.7 and 163.7 ppm).

Similar epoxidation of alkylidene Meldrum's acids (**1b-n**) with hydrogen peroxide gave the corresponding epoxides (**2b-n**) as good crystalline products. Their reaction times and yields are described in Runs 2-15 of Table 1. In the ^{13}C nmr spectra, the two carbonyl carbons of the symmetrical epoxides (**2b-d**, **2h-j**, and **2l-n**) were observed as one signal at δ *ca.* 162 ppm.

Next, in a similar manner to that described for the epoxidation of **1a**, arylidene Meldrum's acids (**3a-l**), which are relatively strong organic Lewis acids (pK_L 4.0~6.2 in 80 vol% methanol),[13] readily reacted with hydrogen peroxide to afford the corresponding epoxides (**4a-l**) in good yields (Runs 16-28 in Table 1). For the epoxidation of **3d**, **3g**, and **3j**, these Meldrum's acids were reacted for 1 or 5 min at 50 °C in a mixture of hydrogen peroxide and acetonitrile, and then the solutions were stirred for 15 or 20 min at room temperature to afford the epoxides (**4d**, **4g**, and **4j**).

The structures of these epoxides (**4a-l**) were also determined from their spectroscopic data. In the ^1H nmr spectra, the 2-methine proton of the *ortho*-substituted aromatic epoxides (**4b**, **4e**, and **4h**) appeared at a lower magnetic field (δ 4.97~5.29 ppm) than those of the other *metha*- or *para*-substituted aromatic epoxides (δ 4.60~4.78 ppm) because of the deshielding effect by the *ortho*-substituent. Moreover, in the ms spectra, though the molecular ion peaks M^+ of the nitrophenyl epoxides (**4h-j**) were not detected, for the other aryl epoxides (**4a-g**, **4k**, and **4l**), molecular ion peaks could be measured.

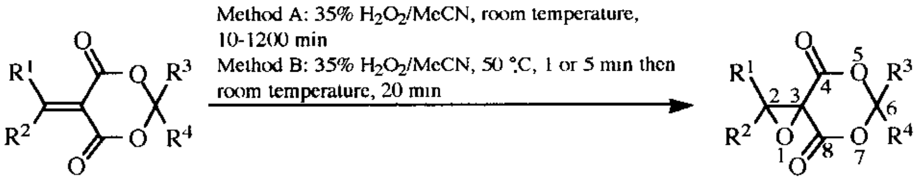


Table 1. Epoxidation of 5-Methylene-1,3-dioxane-4,6-diones with Hydrogen Peroxide in Acetonitrilea)

Run	Substrate	R^1	R^2	R^3	R^4	Reaction time/min	Epoxide	Yield/%
1	**1a**	*i*-Pr	H	Me	Me	10a)	**2a**	76
2	**1b**	Me	Me	Me	Me	30a)	**2b**	69
3	**1c**	$-(CH_2)_4-$		Me	Me	1200a)	**2c**	74
4	**1d**	$-(CH_2)_5-$		Me	Me	180a)	**2d**	37
5	**1e**	*i*-Bu	H	Me	Me	15a)	**2e**	29
6	**1f**	*c*-C_6H_{11}	H	Me	Me	10a)	**2f**	67
7	**1g**	*i*-Pr	H	$-(CH_2)_4-$		10a)	**2g**	74
8	**1h**	Me	Me	$-(CH_2)_4-$		30a)	**2h**	15
9	**1i**	$-(CH_2)_4-$		$-(CH_2)_4-$		60a)	**2i**	40
10	**1j**	$-(CH_2)_5-$		$-(CH_2)_4-$		40a)	**2j**	57
12	**1k**	*i*-Pr	H	$-(CH_2)_5-$		10a)	**2k**	76
13	**1l**	Me	Me	$-(CH_2)_5-$		15a)	**2l**	53
14	**1m**	$-(CH_2)_4-$		$-(CH_2)_5-$		90a)	**2m**	49
15	**1n**	$-(CH_2)_5-$		$-(CH_2)_5-$		40a)	**2n**	37
16	**3a**	Ph	H	Me	Me	10a)	**4a**	54
17	**3b**	$\text{2-BrC}_6\text{H}_4$	H	Me	Me	25a)	**4b**	58
18	**3c**	$\text{3-BrC}_6\text{H}_4$	H	Me	Me	25a)	**4c**	74
19	**3d**	$\text{4-BrC}_6\text{H}_4$	H	Me	Me	21b)	**4d**	52
20	**3e**	$\text{2-ClC}_6\text{H}_4$	H	Me	Me	20a)	**4e**	43
21	**3f**	$\text{3-ClC}_6\text{H}_4$	H	Me	Me	25a)	**4f**	77
22	**3g**	$\text{4-ClC}_6\text{H}_4$	H	Me	Me	25b)	**4g**	61
22	**3h**	$\text{2-NO}_2\text{C}_6\text{H}_4$	H	Me	Me	480a)	**4h**	69
23	**3i**	$\text{3-NO}_2\text{C}_6\text{H}_4$	H	Me	Me	20a)	**4i**	75
24	**3j**	$\text{4-NO}_2\text{C}_6\text{H}_4$	H	Me	Me	25b)	**4j**	75
25	**3k**	$\text{3-MeOC}_6\text{H}_4$	H	Me	Me	35a)	**4k**	76
26	**3l**	$\text{3-MeC}_6\text{H}_4$	H	Me	Me	25a)	**4l**	63

a) Reactions were carried out in a mixture of 35% hydrogen peroxide (3 ml, 35 mmol) and acetonitrile (17 ml or 37 ml) at room temperature under an argon atmosphere. b) Substrate was reacted for 1 or 5 min at 50 °C in a mixture of 35% hydrogen peroxide (3 ml, 35 mmol) and acetonitrile (17 ml or 37 ml) and the solution was then stirred at room temperature.

Since the epoxidation with hydrogen peroxide in acetonitrile is possible to proceed *via* peroxycarboximidic acid,[2,18] we have examined the solvent effects on the epoxidation of **1a** and **3a** using several other solvents in order to clarify this question. The epoxidation in methanol or *tert*-butyl alcohol as a solvent rapidly proceeded leading to the corresponding epoxides (Table 2). However, the epoxidation of the two-phase system between benzene and water proceeded quite slowly, although these conditions eventually produced complete oxidation (Table 2). The results of these solvent effects suggest that the epoxidation of **1a-n** and **3a-l** occurred directly between them and hydrogen peroxide.

Table 2. Solvent Effect on Epoxidation of Isobutylidene Meldrum's Acid and Benzylidene Meldrum's Acid with Hydrogen Peroxide[a)]

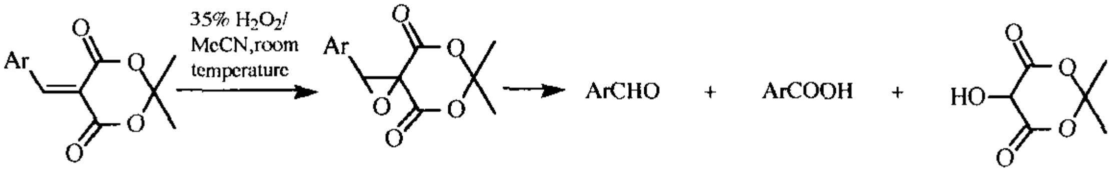
Substrate	Solvent	Time	Yield of epoxide/%
1a	Methanol	10 min	62
	tert-Butyl alcohol	10 min	88
	Benzene[b)]	22 h	85
3a	Methanol	10 min	62
	tert-Butyl alcohol	10 min	75
	Benzene[b)]	24 h	78

a) All reaction were carried out in the presence of **1a** or **3a** (7 mmol) and 35% hydrogen peroxide (3 ml, 35 mmol) in solvent (17 ml). b) Two-phase system.

Arylidene Meldrum's acids (**3m-p**) have an electron donating group such as a methyl or methoxyl group at the *ortho*- or *para*-position, with which a reaction with hydrogen peroxide was tried. In the reactions of **3m-o** with hydrogen peroxide, when the acylals were consumed over 50%, the expected epoxides (**4m-o**) were obtained in low yields.[19] Moreover, when the reactions were allowed to continue, the acylals slowly hydroxylated to yield the corresponding benzaldehydes (**5a-c**) and hydroxy Meldrum's acid (**7**). Moreover, the resulting benzaldehydes (**5a-c**) were oxidized by hydrogen peroxide to yield benzoic acids (**6a-c**). These reactions were supported from observations of ^{1}H nmr in acetonitrile-d_3. This result indicates that the epoxides (**4m-o**) are less labile than the other epoxides (**2a-n**) and (**4a-l**). On the other hand, from the reaction of **3p** with hydrogen peroxide, the expected epoxide **4p** was not obtained and no formation of **4p** was also found from the observation of ^{1}H nmr.

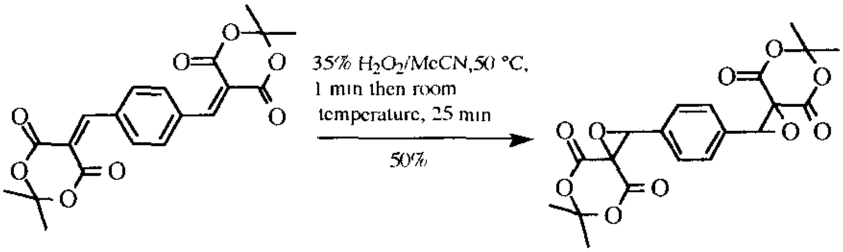
Such a similar tendency using the substituted effect on the aromatic ring of the arylidene Meldrum's acid has been found from the Diels-Alder reaction with 2,3-dimethylbutadiene.[20] These acylals (**3m-p**) whose acidities are in the range of pK_L 6.4 to 7.1 in 80 vol% methanol, are weaker organic Lewis acids than **3a-l**; in particular **3p** (pK_L 7.1) has the most weak acidity in these arylidene acylals.[13] However, the formations of the epoxides (**4m-

o), the substituted benzaldehydes (**5a-d**) and **7** are indicated to undergo nucleophilic attack on the C=C bond of **3m-p** by hydrogen peroxide. Moreover, the alkylidene Meldrum's acids (**1a-d**) having a pK_L of 6.3~8.8 in 80 vol% methanol were readily epoxidized by hydrogen peroxide. Consequentially, it is considered that the epoxidation of **1a-l** and **3a-o** was initiated by the addition of hydrogen peroxide on the methylene moiety of the acylals to give peroxyadducts of the Michael type, which underwent the cyclization to give the epoxide. However, because the hydrolysis of **4m-o** occurs in much faster rate than that of other epoxides, the degradation products are formed. Moreover, in the case of **3p**, it seems that **5d** and **7** are derived from the C-C cleavage of the peroxyadduct or from the hydrolysis of **4p** takes place in much more fast rate than that of **4m-o**.



3	4	5	6	7
m; Ar=2-MeC_6H_4	**m**; Ar=2-MeC_6H_4	**a**; Ar=2-MeC_6H_4	**a**; Ar=2-MeC_6H_4	
n; Ar=4-MeC_6H_4	**n**; Ar=4-MeC_6H_4	**b**; Ar=4-MeC_6H_4	**b**; Ar=4-MeC_6H_4	
o; Ar=2-$MeOC_6H_4$	**o**; Ar=2-$MeOC_6H_4$	**c**; Ar=2-$MeOC_6H_4$	**c**; Ar=2-$MeOC_6H_4$	
p: Ar=4-$MeOC_6H_4$	**p**; Ar=4-$MeOC_6H_4$	**d**; Ar=4-$MeOC_6H_4$	**d**; Ar=4-$MeOC_6H_4$	

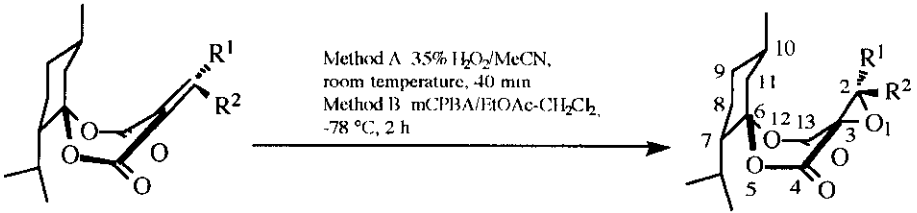
In the cases of alkylidenemalonates, the compound analogous to methylene Meldrum's acids, diethyl ethylidenemalonate, has been epoxidized with alkaline hydrogen peroxide,[2c] while no diethyl isopropylidenemalonate was epoxidized with alkaline hydrogen peroxide,[2e] which has been accomplished by using peroxytrifluoroacetic acid.[6e] In addition, Eberle and Lawton have reported that a thioether, which is a Michael adduct of propylidene Meldrum's acid with thiophenol, was oxidized by hydrogen peroxide leading to the epoxide.[21] However, the epoxidation of **1a-n** and **3a-l** with hydrogen peroxide alone took place completely and those are more reactively than that of ordinary olefins.



8 **9**

For the epoxidation of **8**, the acylal was dissolved for 1 min at 50 °C in a mixture of 35% hydrogen peroxide and acetonitrile and then the solution was stirred at room temperature. After 15 min, a diepoxide (**9**) was depositing as colorless crystals, and, with further stirring for 10 min, was obtained in 50% yield.

Recently, Sato *et al.* have reported asymmetric syntheses using the chiral arylidene Meldrum's acids (**11**).[22-24] The reaction with diazomethane in EtOAc-ether at -78 °C affords the (*S*)-chiral cyclopropane from (*Z*)-form (**11a-*Z***) and the (*R*)-chiral cyclopropane from (*Z*)-form (**11b-*E***), whereas the reaction at room temperature leads to the (*S*)- and (*R*)-chiral cyclopropane mixture, but no other diastereomers were obtained.[22] These acylals in solution undergo a *E-Z* geometrical isomerization on the benzylidene moieties at room temperature, but the isomerization is prohibited at -78 °C and their 1,3-dioxane-4,6-dione ring system has a boat conformation. Hence, diazomethane attacks the methylene moiety on the side of less steric hindrance of the chiral acylal under both conditions of -78 °C and room temperature to yield the chiral cyclopropanes.



11

a-*Z*: R^1=4-$NO_2C_6H_4$, R^2=H
a-*E*: R^1=H, R^2=4-$NO_2C_6H_4$
b-*E*: R^1=H, R^2=4-ClC_6H_4
b-*Z*: R^1=4-ClC_6H_4, R^2=H

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a-*S*: R^1=4-$NO_2C_6H_4$, R^2=H
a-*R*: R^1=H, R^1=4-$NO_2C_6H_4$
b-*R*: R^1=H, R^2=4-ClC_6H_4,
b-*S*: R^1=4-ClC_6H_4, R^2=H

Table 3. Preparation of Chiral Epoxides

Substrate	Method	Products (Isolated Yield/%)			
11a-*Z* + **11a-*E***	A[a,b]	**12a-*S***	(17)	**12a-*R***	(15)
11a-*Z*	B[c,d]		(92)		
11b-*E* + **11b-*Z***	A[a,b]	**12b-*S***	(28)	**12b-*R***	(28)
11b-*E*	B[c,d]				(71)

a) Epoxidation was carried out in a mixture of acetonitrile and 35% hydrogen peroxide at room temperature b) The epoxides were separately isolated by silica gel chromatography. c) Epoxidation was carried out in a mixture of ethyl acetate and dichloromethane in the presence of mCPBA at -78 °C d) The epoxide was purified by recrystallization from ether.

It is considered that such asymmetric syntheses are applicable to the epoxidation of the chiral arylidene Meldrum's acid (**11**). Next we then studied the epoxidation of **11**.

The reaction of a mixture of chiral (*Z*)- and (*E*)-4-nitrobenzylidene Meldrum's acids (**11a-*Z*** and **11a-*E***) with 35% hydrogen peroxide in acetonitrile at room temperature gave two chiral epoxides (**12a-*S*** and **12a-*R***; *ca.* 1:1

ratio by ^{1}H nmr), which were readily isolated by silica gel chromatography. Optical rotations of the first eluted and the next eluted epoxides have positive [$[\alpha]_D^{12}$ +155° (*c* 1.03, acetone)] and negative [$[\alpha]_D^{13}$ -91° (*c* 1.04, acetone)] values, respectively. The mp's and optical rotation values by repeated recrystallization of the epoxides (**12a**-*S* and **12a**-***R***) did not change and the ^{1}H nmr spectra using a chiral reagent, tris[3-(heptafluoropropylhydroxymethylene)-*d*-camphorato]europium (III), showed the absence of a chiral isomer. Because no atoms possessed an anomalous scattering effect, absolute configurations for these epoxides were not made from an X-ray crystallographic analysis. Menthylidene moieties in these epoxides, however, will be optically pure, hence, on the basis of the structure of *l*-menthylidene group, apparently the first eluted epoxide is a (2*R*,3*S*,6*R*,7*S*,10*R*)-form (**12a-*R***), whereas the next eluted epoxide is a (2*S*,3*S*,6*S*,7*S*,10*R*)-form (**12a**-*S*) (Figures 1 and 2).

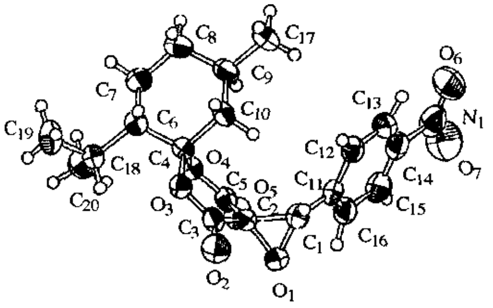


Figure 1. ORTEP drawing of **12a**-*S*

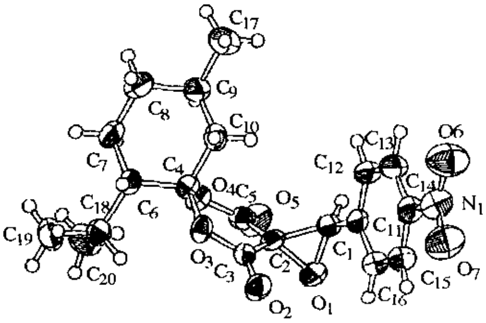
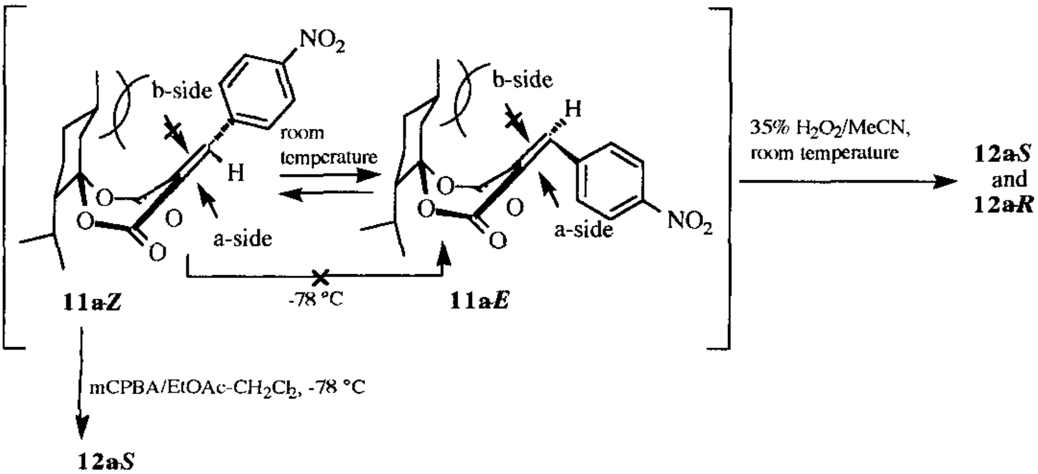


Figure 2. ORTEP drawing of **12a**-***R***

Similar epoxidation of a mixture of chiral (*E*)- and (*Z*)-4-chlorobenzylidene Meldrum's acids (**11b-*E*** and **11d-*Z***) gave epoxides (**12b-*R*** and **12b**-*S*), which were also readily isolated by silica gel chromatography. The optical rotation values of **12b-*R*** and **12b**-*S* have $[\alpha]_D^{21}$ +150° (*c* 1.54, acetone) and $[\alpha]_D^{22}$ -87° (*c* 0.51, acetone), respectively, which are close to those of the 4-nitrophenyl epoxides (**12a-*R*** and **12a**-*S*).[25]

The pure chiral arylidene Meldrum's acids (**11a-*Z*** and **11b**-*E*) are readily obtained by slowly recrystallization from ether in the (*E*)- and (*Z*)-isomer mixture.[22] However, **11a-Z** and **11b**-*E* isomerize to the corresponding (*E*)- or (*Z*)-form at room temperature in solution to afford the 1:1 equilibrium mixture of the (*E*)- and (*Z*)-forms. Therefore, it is considered that the epoxidations of the pure chiral acylals require a low temperature condition such as the above cyclopropanation with diazomethane.[22] Because 35% hydrogen peroxide, which is frozen at -78 °C, is unsuitable as the oxidant, mCPBA was used as the oxidant in EtOAc-CH_2Cl_2. While the epoxidation of the (*Z*)-form (**11a-*Z***) with mCPBA led to **12a**-*S*, that of the (*E*)-form (**11b**-*E*) gave **12b-*R*** (Table 3).

Analogous to the reaction of the chiral acylals with diazomethane, the results of these epoxidations with hydrogen peroxide or mCPBA indicate that the epoxidation by hydrogen peroxide or mCPBA occurs only on the a-sides of the benzylidene moiety.



In summary, a simple and high yield method for the synthesis of spiro epoxides has been developed. Additionally, the epoxidation of the chiral arylidene Meldrum's acids with hydrogen peroxide gave two diastereomers whose purification by silica gel chromatography ensures 100% optical purity. In addition, when mCPBA was used as the oxidant at -78 °C, the diastereoselective epoxidation takes place.

EXPERIMENTAL

Melting points were determined on a micro hot-stage (Yazawa) and are uncorrected. Ir spectra were taken as KBr disks or a liquid film inserted NaCl plates using a BIO-RAD FTS-60A spectrophotometer. Nmr spectra were measured in $CDCl_3$, DMSO-d_6 or acetonitrile-d_3 with TMS as internal standard using a JEOL JNM-EX90 spectrometer (90 MHz for ^1H and 22.5 MHz for ^{13}C). LRms and HRms spectra were obtained with a JEOL JNM-AX-500 spectrometer using a direct insertion probe at an ionization voltage 70 eV. Optical rotations were measured on a JASCO DIP-181 polarimeter. Elemental analyses were obtained using a Perkin-Elmer 240C element analyzer. The silica gel used was Merck (9385) silica gel 60. Analytical tlc used was Merck (5714) silica gel $60F_{254}$ glass-backed plates. Tris[3-(heptafluoropropylhydroxymethylene)-*d*-camphorato]europium (III) was purchased from Fluka Chemie AG. Methylene Meldrum's acids (**1a-n**, **3a-q**, and **8**; except **1e**, **1h**, and **1l**) were prepared according to published procedures.[11,13] The chiral arylidene Meldrum's acids [**11a-*Z***: mp 148 °C (ether), lit.,[22] mp 147-149 °C and **11b-*E***: mp 135-136 °C (ether), lit.,[22] mp 132-134 °C] were prepared using a literature method.

*5-Isopentylidene-2,2-dimethyl-1,3-dioxane-4,6-dione (**1e**).* To a solution of isovaleraldehyde (4.5 g, 52 mmol) and Meldrum's acid (7.2 g, 50 mmol) in benzene (250 ml) was added piperidine (0.1 g) and acetic acid (0.1 g). The mixture was refluxed for 3 h in a water bath, then cooled, washed with 0.1 mol l^{-1} HCl (100 ml), dried ($MgSO_4$), and evaporated *in vacuo* to give a crude oil, which was chromatographed on a silica gel column using acetone/hexane (5/95, *v/v*) as an eluent to yield **1e**: a colorless oil; ^1H nmr ($CDCl_3$) δ 1.02 (6H, d, *J*=6.3 Hz), 1.74 (6H, s), 1.94 (1H, m), 2.85 (2H, dd, *J*=5.6 and 7.5 Hz), 7.89 (1H, t, *J*=7.5 Hz). *Anal.* Calcd for $C_{11}H_{16}O_4$: C, 62.25; H, 7.60. Found: C, 61.91; H, 7.59.

*General Procedure for Isopropylidene Spirocyclic Acylals (**1h** and **1l**).* A solution of 6,10-dioxaspiro[4.5]decane-7,9-dione[11] or 1,5-dioxaspiro[5.5]undecane-2,4-dione[11] (30 mmol) and acetone (1.9 g, 32 mmol) in pyridine (7 ml) was stirred at room temperature under an argon atmosphere for 24 h. The solvent was removed under vacuum below 40 °C and the residue was poured into cold water (20 ml) to give crude crystals, from which cyclic acylals were obtained by recrystallization from methanol/water.

*8-Isopropylidene-6,10-dioxaspiro[4.5]decane-7,9-dione (**1h**).* Yield 1.6 g (25%); mp 91-94 °C; ir (KBr) 1752, 1728, 1610 cm^{-1}; ^1H nmr ($CDCl_3$) δ 1.73-2.37 (8H, m), 2.45 (6H, s). *Anal.* Calcd for $C_{11}H_{14}O_4$: C, 62.85; H, 6.71. Found: C, 62.78; H, 6.64.

*3-Isopropylidene-1,5-dioxaspiro[5.5]undecane-2,4-dione (**1l**).* Yield 1.4 g (21%); mp 103-104 °C; ir (KBr) 1760, 1728, 1606 cm^{-1}; ^1H nmr ($CDCl_3$) δ 1.33-2.10 (10H, m), 2.52 (6H, s). *Anal.* Calcd for $C_{12}H_{16}O_4$: C, 64.27; H, 7.19. Found: C, 64.24; H, 7.12.

*Epoxidation of Isobutylidene Meldrum's Acid (**1a**) with Hydrogen Peroxide. In Acetonitrile:* To a solution of **1a** (1.44 g, 7.27 mmol) in acetonitrile (17 ml) was added 35% hydrogen peroxide (3 ml, 35 mmol) at room temperature under an argon atmosphere. The mixture was stirred for 10 min, then 10% $NaHSO_3$ (20 ml) was added, and extracted with CH_2Cl_2 (20 ml × 2). The organic fractions were combined, dried over $MgSO_4$, evaporated *in vacuo* to afford crude crystals, from which 2-isopropyl-6,6-dimethyl-1,5,7-trioxaspiro[2.5]octane-4,8-dione (**2a**) was obtained by recrystallization from ether/hexane: yield 1.19 g (76%); colorless crystals; mp 73-74 °C; ir (KBr) 1786, 1763 cm^{-1}; ^1H nmr ($CDCl_3$) δ 1.01 (3H, d, *J*=7.1 Hz), 1.20 (3H, d, *J*=7.1 Hz), 1.82 (3H, s), 1.85 (3H, s), 1.99 (1H, d septet, *J*=9.3 and 7.1 Hz), 3.43 (1H, d, *J*=9.3 Hz); ^{13}C nmr ($CDCl_3$) δ 18.3 (q), 19.9 (q), 26.4 (d), 27.6 (q), 28.3 (q), 55.4 (s, 3-C), 75.5 (d, 2-C), 105.9 (s, 6-C), 161.7 (s, COO), 163.7 (s, COO). *Anal.* Calcd for $C_{10}H_{14}O_5$: C, 56.07; H, 6.59. Found: C, 56.07; H, 6.71.

In Methanol or tert-Butyl Alcohol: The epoxidation of **1a** (7 mmol) in methanol or *tert*-butyl alcohol (17 ml) with 35% hydrogen peroxide (3 ml, 35 mmol) was carried out using the above similar method. The yields are summarized in Table 2.

In Benzene: To a solution of **1a** (1.39 g, 7.02 mmol) in benzene (17 ml) was added 35% hydrogen peroxide (3 ml, 35 mmol). The suspension was vigorously stirred for 22 h at room temperature, then quenched with 10% $NaHSO_3$ (20 ml) and extracted with CH_2Cl_2 (20 ml × 2). The extracts were dried over $MgSO_4$ and evaporated *in vacuo*. The residue was recrystallized from ether/hexane to give **2a** (1.28 g, 85%).

*Epoxidation of 5-Alkylidene-1,3-dioxane-4,6-diones (**1b-n**) with Hydrogen Peroxide.* The epoxidation of **1b-n** was carried out using the method of **1a** in acetonitrile. The yields and reaction times are summarized in Table 1. Physical and analytical data are as follows.

*2,2,6,6-Tetramethyl-1,5,7-trioxaspiro[2.5]octane-4,8-dione (**2b**).* Colorless crystals; mp 124 °C (from CH_2Cl_2/hexane); ir (KBr) 1798, 1763 cm^{-1}; ^1H nmr ($CDCl_3$) δ 1.58 (6H, s), 1.80 (3H, s), 1.83 (3H, s); ^{13}C nmr ($CDCl_3$) δ 18.9 (q, 2C), 27.0 (q), 27.7 (q), 61.6 (s, 3-C), 70.7 (s, 2-C), 105.2 (s, 6-C), 162.4 (s, 2C, COO × 2). *Anal.* Calcd for $C_9H_{12}O_5$: C, 54.00; H, 6.04. Found: C, 53.95; H, 5.85.

*9,9-Dimethyl-8,10,12-trioxadispiro[4.0.5.1]dodecane-7,11-dione (**2c**).* Colorless crystals; mp 116-117 °C (from benzene/hexane); ir (KBr) 1791, 1767 cm^{-1}; ^1H nmr ($CDCl_3$) δ 1.5-2.3 (8H, m, CH_2 × 4), 1.79 (3H, s), 1.83 (3H, s); ^{13}C nmr ($CDCl_3$) δ 24.9 (t, 2C), 27.6 (q), 27.8 (q), 30.2 (t, 2C), 60.4 (s, 6-C), 81.2 (s, 5-C), 105.4 (s, 9-C), 162.6 (s, 2C, COO × 2). *Anal.* Calcd for $C_{11}H_{14}O_5$: C, 58.40; H, 6.24. Found: C, 58.38; H, 6.10.

*3,3-Dimethyl-2,4,13-trioxadispiro[5.0.5.1]tridecane-1,5-dione (**2d**).* Colorless crystals; mp 133 °C (from benzene/hexane); ir (KBr) 1796, 1769 cm^{-1}; ^1H nmr ($CDCl_3$) δ 1.3-2.1 (16H, m, CH_2 × 5 and CH_3 × 2); ^{13}C nmr ($CDCl_3$) δ 24.7 (t, 2C), 25.0 (t), 27.0 (q), 27.7 (q), 28.6 (t, 2C), 62.3 (s, 7-C), 75.4 (s, 6-C), 105.1 (s, 10-C), 162.1 (s, 2C, COO × 2). *Anal.* Calcd for $C_{12}H_{16}O_5$: C, 59.99; H, 6.71. Found: C, 59.86; H, 6.59.

*2-Isobutyl-6,6-dimethyl-1,5,7-trioxaspiro[2.5]octane-4,8-dione (**2e**).* Colorless crystals; mp 77-78 °C (from benzene/hexane); ir (KBr) 1788, 1764 cm^{-1}; ^1H nmr ($CDCl_3$) δ 1.04 (3H, d, J=6.6 Hz), 1.06 (3H, d, J=6.6 Hz), 1.6-2.1 (3H, m, $CHCH_2$), 1.84 (6H, s), 3.68 (1H, dd, J=4.9 and 6.1 Hz); ^{13}C nmr ($CDCl_3$) δ 22.3 (q), 22.5 (q), 26.6 (d), 27.6 (q), 28.0 (q), 35.2 (t), 54.9 (s, 3-C), 67.6 (d, 2-C), 105.8 (s, 6-C), 161.8 (s, COO), 163.8 (s, COO). *Anal.* Calcd for $C_{11}H_{16}O_5$: C, 57.88; H, 7.07. Found: C, 58.09; H, 6.97.

*2-Cyclohexyl-6,6-dimethyl-1,5,7-trioxaspiro[2.5]octane-4,8-dione (**2f**).* Colorless crystals; mp 75-78 °C (from benzene/hexane); ir (KBr) 1794, 1764 cm^{-1}; ^1H nmr ($CDCl_3$) δ 0.9-2.2 (11H, m, CH_2 × 5 and CH), 1.84 (3H, s), 1.88 (3H, s), 3.42 (1H, d, J=8.4 Hz); ^{13}C nmr ($CDCl_3$) δ 24.9 (t), 25.7 (t), 27.7 (t), 28.4 (q), 28.6 (t), 30.1 (t), 35.4 (d), 55.0 (s, 3-C), 72.4 (d, 2-C), 106.0 (s, 6-C), 161.8 (s, COO), 163.8 (s, COO). *Anal.* Calcd for $C_{13}H_{16}O_5$: C, 61.41; H, 7.02. Found: C, 61.24; H, 7.02.

*2-Isopropyl-1,5,11-trioxadispiro[2.2.4.2]dodecane-4,12-dione (**2g**).* Colorless crystals; mp 74 °C (from benzene/hexane); ir (KBr) 1799, 1766 cm^{-1}; ^1H nmr ($CDCl_3$) δ 1.03 (3H, d, J=6.7 Hz), 1.21 (3H, d, J=6.7 Hz), 1.7-2.5 (9H, m, CH_2 × 4 and CH), 3.38 (1H, d, J=8.8 Hz); ^{13}C nmr ($CDCl_3$) δ 18.4 (q), 19.9 (q), 22.3 (t), 24.1 (t), 26.5 (d), 38.2 (t), 39.8 (t), 56.1 (s, 3-C), 73.5 (d, 2-C), 114.8 (s, 6-C), 162.2 (s, COO), 164.0 (s, COO). *Anal.* Calcd for $C_{12}H_{16}O_5$: C, 59.99; H, 6.71. Found: C, 60.11; H, 6.63.

*2,2-Dimethyl-1,5,11-trioxadispiro[2.2.4.2]dodecane-4,12-dione (**2h**).* Colorless crystals; mp 124 °C (from benzene/hexane); ir (KBr) 1787, 1761 cm^{-1}; ^1H nmr ($CDCl_3$) δ 1.58 (6H, s), 1.7-2.5 (8H, m, CH_2 × 4); ^{13}C nmr ($CDCl_3$) δ 19.0 (q, 2C), 22.8 (t), 24.6 (t), 38.5 (t), 39.2 (t), 62.3 (s, 3-C), 70.7 (d, 2-C), 114.2 (s, 6-C), 163.0 (s, 2C, COO × 2). *Anal.* Calcd for $C_{11}H_{14}O_5$: C, 58.40; H, 6.23. Found: C, 58.54; H, 6.18.

7,13,15-Trioxatrispiro[4.0.2.4.2.1]hexadecane-6,14-dione (2i). Colorless crystals; mp 145-146 °C (from benzene/hexane); ir (KBr) 1788, 1764 cm^{-1}; ^{1}H nmr (CDCl$_3$) δ 1.5-2.5 (16H, m, CH$_2$ × 8); ^{13}C nmr (CDCl$_3$) δ 22.8 (t), 24.6 (t), 24.9 (t, 2C), 30.2 (t, 2C), 38.4 (t), 39.7 (t), 61.0 (s, 6-C), 81.2 (s, 5-C), 114.4 (s, 9-C), 163.2 (s, 2C, COO × 2). *Anal.* Calcd for $C_{13}H_{16}O_5$: C, 61.90; H, 6.39. Found: C, 61.73; H, 6.40.

6,15,17-Trioxatrispiro[4.2.0.5.1.2]heptadecane-7,16-dione (2j). Colorless crystals; mp 148-152 °C (from ether/hexane); ir (KBr) 1792, 1760 cm^{-1}; ^{1}H nmr (CDCl$_3$) δ 1.2-2.5 (18H, m, CH$_2$ × 9); ^{13}C nmr (CDCl$_3$) δ 22.8 (t), 24.6 (t, 2C), 24.7 (t), 25.0 (t), 28.7 (t, 2C), 38.6 (t), 39.2 (t), 63.1 (s, 8-C), 75.5 (s, 9-C), 114.2 (s, 5-C), 162.7 (s, 2C, COO × 2). *Anal.* Calcd for $C_{14}H_{18}O_5$: C, 63.15; H, 6.81. Found: C, 62.99; H, 6.70.

2-Isopropyl-1,5,12-trioxadispiro[2.2.5.2]tridecane-4,13-dione (2k). Colorless crystals; mp 96-98 °C (from benzene/hexane); ir (KBr) 1792, 1764 cm^{-1}; ^{1}H nmr (CDCl$_3$) δ 0.99 (3H, d, J=6.6 Hz), 1.21 (3H, d, J=6.6 Hz), 1.3-2.4 (11H, m, CH$_2$ × 5 and CH), 3.38 (1H, d, J=8.8 Hz); ^{13}C nmr (CDCl$_3$) δ 17.7 (q), 19.6 (q), 21.4 (t), 22.0 (t), 23.4 (t), 26.1 (d), 35.4 (t), 37.0 (t), 55.2 (s, 3-C), 72.9 (d, 2-C), 106.4 (s, 6-C), 161.3 (s, COO), 163.3 (s, COO). *Anal.* Calcd for $C_{13}H_{18}O_5$: C, 61.41; H, 7.13. Found: C, 61.16; H,7.02.

2,2-Dimethyl-1,5,12-trioxadispiro[2.2.5.2]tridecane-4,13-dione (2l). Colorless crystals; mp 136-137 °C (from benzene/hexane); ir (KBr) 1788, 1757 cm^{-1}; ^{1}H nmr (CDCl$_3$) δ 1.3-2.2 (10H, m, CH$_2$ × 5), 1.56 (6H, s); ^{13}C nmr (CDCl$_3$) δ 18.9 (q, 2C), 21.8 (t), 22.5 (t), 23.9 (t), 36.1 (t), 36.4 (t), 61.8 (s, 3-C), 70.6 (s, 2-C), 106.0 (s, 6-C), 162.4 (s, 2C, COO × 2). *Anal.* Calcd for $C_{12}H_{16}O_5$: C, 59.99; H, 6.71. Found: C, 59.91; H, 6.68.

8,15,17-Trioxatrispiro[4.0.2.5.2.1]heptadecane-7,16-dione (2m). Colorless crystals; mp 148-149 °C (from benzene/hexane); ir (KBr) 1792, 1762 cm^{-1}; ^{1}H nmr (CDCl$_3$) δ 1.3-2.3 (18H, m, CH$_2$ × 9); ^{13}C nmr (CDCl$_3$) δ 21.7 (t), 22.5 (t), 23.9 (t), 24.9 (t, 2C), 30.2 (t, 2C), 36.0 (t), 37.2 (t), 60.5 (s, 6-C), 81.1 (s, 5-C), 106.2 (s, 9-C), 162.7 (s, 2C, COO × 2). *Anal.* Calcd for $C_{14}H_{18}O_5$: C, 63.15; H, 6.81. Found: C, 62.80; H, 6.74.

9,16,18-Trioxatrispiro[5.0.2.5.2.1]octadecane-8,17-dione (2n). Colorless crystals; mp 158-160 °C (from benzene/hexane); ir (KBr) 1786, 1758 cm^{-1}; ^{1}H nmr (CDCl$_3$) δ 1.2-2.2 (20H, m, CH$_2$ × 10); ^{13}C nmr (CDCl$_3$) δ 21.8 (t), 22.5 (t), 23.9 (t), 24.8 (t, 2C), 25.1 (t), 28.6 (t, 2C), 36.4 (t), 36.1 (t), 62.4 (s, 7-C), 75.2 (s, 6-C), 106.0 (s, 9-C), 162.2 (s, 2C, COO × 2). *Anal.* Calcd for $C_{15}H_{20}O_5$: C, 64.27; H, 7.19. Found: C, 64.00; H, 7.20.

6,6-Dimethyl-1,5,7-trioxa-2-phenylspiro[2.5]octane-4,8-dione (4a). In Acetonitrile: To a solution of benzylidene Meldrum's acid (**3a**; 1.17 g, 5.04 mmol) in acetonitrile (17 ml) was added 35% hydrogen peroxide (3 ml, 35 mmol) at room temperature under an argon atmosphere. The mixture was stirred for 10 min and then 10% NaHSO$_3$ (20 ml) added. The solution was extracted with CH$_2$Cl$_2$ (20 ml × 2) and the combined organic fractions were dried over MgSO$_4$ and evaporated *in vacuo* to afford crude crystals, which were recrystallized from benzene/hexane to give **4a** (675 mg, 54%) as colorless crystals. This compound melted at 90 °C and decomposed at 126 -132 °C; ir (KBr) 1801, 1771 cm^{-1}; ^{1}H nmr (CDCl$_3$) δ 1.76 (6H, s), 4.64 (1H, s, 2-CH), 7.2-7.7 (5H, m, ArH); ^{13}C nmr (DMSO-d_6) δ 27.0 (q), 27.7 (q), 58.8 (s, 3-C), 66.8 (d, 2-C), 105.7 (s, 6-C), 127.7 (d, 2C), 128.0 (d, 2C), 129.7 (s and d, 2C), 159.8 (s, COO), 162.7 (s, COO); LRms m/z (rel. intensity) 248 (M$^+$; 4), 105(100). *Anal.* Calcd for $C_{13}H_{12}O_5$: C, 62.90; H, 4.87. Found: C, 62.73; H, 4.89.

In Methanol or tert-Butyl Alcohol: The epoxidation of **3a** (7 mmol) in methanol or *tert*-butyl alcohol (17 ml) with 35% hydrogen peroxide (3 ml, 35 mmol) was carried out using the above similar method. The yields are summarized in Table 2.

In Benzene: To a solution of **3a** (1.62 g, 7.00 mmol) in benzene (17 ml) was added 35% hydrogen peroxide (3 ml, 35 mmol). The suspension was vigorously stirred for 24 h at room temperature, then quenched with 10% $NaHSO_3$ (20 ml) and extracted with CH_2Cl_2 (20 ml × 2). The extracts were dried over $MgSO_4$ and evaporated *in vacuo*. The residue was recrystallized from benzene/hexane to give **4a** (1.35 g, 78%).

*2-(2-Bromophenyl)-6,6-dimethyl-1,5,7-trioxaspiro[2.5]octane-4,8-dione (**4b**).* This compound was prepared in a similar manner to that described for **4a** from a solution of **3b** (1.55 g, 5.00 mmol) and 35% hydrogen peroxide (3 ml, 35 mmol) in acetonitrile (17 ml): yield 954 mg (58%); colorless crystals; mp 124-125 °C (from benzene/hexane); ir (KBr) 1794, 1767 cm^{-1}; ^1H nmr ($CDCl_3$) δ 1.80 (3H, s), 1.95 (3H, s), 4.97 (1H, s, 2-CH), 7.1-7.9 (4H, m, ArH); ^{13}C nmr ($CDCl_3$) δ 27.7 (q), 28.6 (q), 57.1 (s, 3-C), 68.0 (d, 2-C), 106.3 (s, 6-C), 122.8 (s), 127.3 (d), 128.4 (s), 130.5 (d), 131.7 (d), 132.5 (d), 159.5 (s, COO), 162.7 (s, COO); LRms *m/z* (rel. intensity) 328 (7), 326 (M^+; 8), 186 (65), 184 (68), 89 (100). *Anal.* Calcd for $C_{13}H_{11}O_5Br$: C, 47.73; H, 3.39. Found: C, 47.46; H, 3.30.

*2-(3-Bromophenyl)-6,6-dimethyl-1,5,7-trioxaspiro[2.5]octane-4,8-dione (**4c**).* This compound was prepared in a similar manner to that described for **4a** from a solution of **3c** (1.56 g, 5.01 mmol) and 35% hydrogen peroxide (3 ml, 35 mmol) in acetonitrile (17 ml): yield 1.21 g (74%); colorless crystals; mp 141-143 °C (from benzene/hexane); ir (KBr) 1799, 1764 cm^{-1}; ^1H nmr ($CDCl_3$) δ 1.75 (3H, s), 1.80 (3H, s), 4.60 (1H, s, 2-CH), 7.2-7.8 (4H, m, ArH); ^{13}C nmr (DMSO-d_6) δ 27.1 (q), 28.0 (q), 58.6 (s, 3-C), 65.8 (d, 2-C), 105.9 (s, 6-C), 121.4 (s), 126.9 (d), 130.3 (d, 2C), 132.4 (s), 132.6 (d), 159.9 (s, COO), 162.5 (s, COO); LRms *m/z* (rel. intensity) 328 (8), 326 (M^+; 7), 186 (94), 184 (93), 89 (100). *Anal.* Calcd for $C_{13}H_{11}O_5Br$: C, 47.73; H, 3.39. Found: C, 47.54; H, 3.33.

*2-(4-Bromophenyl)-6,6-dimethyl-1,5,7-trioxaspiro[2.5]octane-4,8-dione (**4d**).* A suspension of 4-bromobenzylidene Meldrum's acid (**3d**; 1.56 g, 5.01 mmol), 35% hydrogen peroxide (3 ml, 35 mmol) and acetonitrile (37 ml) was stirred all crystals of **3d** dissolved under an argon atmosphere at 50 °C in a water bath (required about 1 min) and further stirred at room temperature for 20 min. To the reaction mixture was added 5% $NaHSO_3$ (40 ml) and the mixture was extracted with CH_2Cl_2 (20 ml × 2). The combined organic fractions were dried over $MgSO_4$ and evaporated *in vacuo* to afford crude crystals, which were recrystallized from benzene/hexane to give **4d** (853 mg, 52%) as colorless crystals; mp 118-120 °C; ir (KBr) 1798, 1764 cm^{-1}; ^1H nmr ($CDCl_3$) δ 1.75 (3H, s), 1.79 (3H, s), 4.61 (1H, s, 2-CH), 7.41 (2H, d, J=9.3 Hz, ArH), 7.57 (2H, d, J=9.3 Hz, ArH); ^{13}C nmr (DMSO-d_6) δ 27.0 (q), 27.8 (q), 58.5 (s, 3-C), 66.1 (d, 2-C), 105.8 (s, 6-C), 123.3 (s), 129.1 (s), 129.9 (d, 2C), 131.1 (d, 2C), 159.8 (s, COO), 162.5 (s, COO); LRms *m/z* (rel. intensity) 328 (8), 326 (M^+; 7), 186 (96), 184 (94), 89 (100). *Anal.* Calcd for $C_{13}H_{11}O_5Br$: C, 47.73; H, 3.39. Found: C, 47.47; H, 3.28.

*2-(2-Chlorophenyl)-6,6-dimethyl-1,5,7-trioxaspiro[2.5]octane-4,8-dione (**4e**).* A stirred suspension of 2-chlorobenzylidene Meldrum's acid (**3e**; 1.34 g, 5.00 mmol) and 35% hydrogen peroxide (3 ml, 35 mmol) in acetonitrile (17 ml) was dissolved for 15 min at room temperature and the solution was further stirred for 5 min. To the reaction mixture was added 10% $NaHSO_3$ (20 ml) and the mixture was extracted with CH_2Cl_2 (20 ml × 2). The combined organic fractions were dried over $MgSO_4$ and evaporated *in vacuo* to afford crude crystals, which were recrystallized from benzene/hexane to give **4e** (614 mg, 43%) as colorless crystals; mp 124-126 °C; ir (KBr) 1798, 1768 cm^{-1}; ^1H nmr ($CDCl_3$) δ 1.81 (3H, s), 1.92 (3H, s), 5.00 (1H, s, 2-CH), 7.3-7.4 (3H, m, ArH), 7.6-7.8 (1H, m, ArH); ^{13}C nmr ($CDCl_3$) δ 27.6 (q), 28.2 (q), 57.2 (s, 3-C), 65.9 (d, 2-C), 106.3 (s, 6-C), 126.8 (d), 126.9 (s), 129.2 (d), 130.2 (d), 131.4 (d), 133.4 (s), 159.4 (s, COO), 162.7 (s, COO); LRms *m/z* (rel. intensity) 282 (M^+; 12), 140 (100), 89 (80). *Anal.* Calcd for $C_{13}H_{11}O_5Cl$: C, 55.24; H, 3.92. Found: C, 55.21; H, 3.94.

*2-(3-Chlorophenyl)-6,6-dimethyl-1,5,7-trioxaspiro[2.5]octane-4,8-dione (**4f**).* This compound was prepared in a manner similar to that described for **4a** from a solution of **3f** (1.33 g, 5.00 mmol) and 35% hydrogen peroxide (3 ml, 35 mmol) in acetonitrile (17 ml): yield 1.10 g (77%); colorless crystals; mp 134-137 °C (from CH_2Cl_2/hexane); ir (KBr) 1800, 1769 cm^{-1}; ^1H nmr ($CDCl_3$) δ 1.78 (3H, s), 1.80 (3H, s), 4.61 (1H, s, 2-CH), 7.37-7.43 (3H, m, ArH), 7.54 (1H, br s, ArH); ^{13}C nmr ($CDCl_3$) δ 27.0 (q), 27.9 (q), 58.5 (s, 3-C), 65.7 (d, 2-C), 105.9 (s, 6-C), 126.5 (d), 127.4 (d), 129.7 (d), 130.0 (s), 132.2 (d), 132.9 (s), 159.8 (s, COO), 162.5 (s, COO); LRms *m/z* (rel. intensity) 282 (M^+; 5), 140 (100), 89 (73). *Anal.* Calcd for $C_{13}H_{11}O_5Cl$: C, 55.24; H, 3.92. Found: C, 55.24; H, 3.93.

*2-(4-Chlorophenyl)-6,6-dimethyl-1,5,7-trioxaspiro[2.5]octane-4,8-dione (**4g**).* A suspension of 4-chlorobenzylidene Meldrum's acid (**3g**; 1.33 g, 5.00 mmol) and 35% hydrogen peroxide (3 ml, 35 mmol) in acetonitrile (37 ml) was stirred until all crystals of **3g** dissolved under an argon atmosphere at 50 °C in a water bath (required about 5 min), and further stirred at room temperature for 20 min. To the reaction mixture was added a 5% $NaHSO_3$ solution (40 ml) and the solution was extracted with CH_2Cl_2 (20 ml × 2). The combined organic fractions were dried over $MgSO_4$ and evaporated *in vacuo* to afford crude crystals, which were recrystallized from benzene/hexane to give **4g** (860 mg, 61%) as colorless crystals; mp 98-99 °C; ir (KBr) 1798, 1765 cm^{-1}; ^1H nmr ($CDCl_3$) δ 1.76 (3H, s), 1.79 (3H, s), 4.63 (1H, s, 2-CH), 7.39 (2H, d, J=9.3 Hz, ArH), 7.52 (2H, d, J=9.3 Hz, ArH); ^{13}C nmr (DMSO-d_6) δ 27.0 (q), 27.8 (q), 58.6 (s, 3-C), 66.1 (d, 2-C), 105.9 (s, 6-C), 128.2 (d, 2C), 128.8 (s), 131.2 (d, 2C), 134.7 (s), 159.9 (s, COO), 162.6 (s, COO); LRms *m/z* (rel. intensity) 282 (M^+; 7), 140 (100), 89 (59). *Anal.* Calcd for $C_{13}H_{11}O_5Cl$: C, 55.24; H, 3.92. Found: C, 55.19; H, 3.99.

*6,6-Dimethyl-2-(2-nitrophenyl)-1,5,7-trioxaspiro[2.5]octane-4,8-dione (**4h**).* To a solution of 2-nitrobenzylidene Meldrum's acid (**3h**; 1.39 g, 5.01 mmol) in acetonitrile (17 ml) was added 35% hydrogen peroxide (3 ml, 35 mmol) at room temperature under an argon atmosphere. The mixture was stirred at room temperature for 8 h and then 10% $NaHSO_3$ solution (20 ml) was added. The solution was extracted with CH_2Cl_2 (20 ml × 2) and the combined organic fractions were dried over $MgSO_4$ and evaporated *in vacuo* to afford crude crystals, which were recrystallized from benzene/hexane to give **4h** (1.01 g, 69%) as colorless crystals; mp 143-145 °C; ir (KBr) 1785, 1760, 1525 (NO_2) cm^{-1}; ^1H nmr ($CDCl_3$) δ 1.83 (3H, s), 1.87 (3H, s), 5.29 (1H, s, 2-CH), 7.5-8.3 (4H, m, ArH); ^{13}C nmr ($CDCl_3$) δ 28.0 (q), 28.2 (q), 56.3 (s, 3-C), 66.0 (d, 2-C), 106.9 (s, 6-C), 125.0 (d), 126.1 (s), 130.9 (d), 131.2 (d), 134.3 (d), 147.3 (s), 160.0 (s, COO), 162.5 (s, COO). *Anal.* Calcd for $C_{13}H_{11}NO_7$: C, 53.26; H, 3.78; N, 4.78. Found: C, 53.16; H, 3.70; N, 4.61.

*6,6-Dimethyl-2-(3-nitrophenyl)-1,5,7-trioxaspiro[2.5]octane-4,8-dione (**4i**).* This compound was prepared in a manner similar to that described for **4a** from a solution of **3i** (1.39 g, 5.01 mmol) and 35% hydrogen peroxide (3 ml, 35 mmol) in acetonitrile (17 ml): yield 1.10 g (75%); colorless crystals; mp 136 °C (decomp.) (from CH_2Cl_2/hexane); ir (KBr) 1794, 1765, 1530 (NO_2) cm^{-1}; ^{1}H nmr ($CDCl_3$) δ 1.81 (6H, s), 4.78 (1H, s, 2-CH), 7.5-8.5 (4H, m, ArH); ^{13}C nmr (DMSO-d_6) δ 27.1 (q), 28.1 (q), 58.3 (s, 3-C), 65.5 (d, 2-C), 106.1 (s, 6-C), 122.6 (d), 124.6 (d), 129.9 (d), 132.1 (s), 134.3 (d), 147.5 (s), 160.1 (s, COO), 162.4 (s, COO). *Anal.* Calcd for $C_{13}H_{11}NO_7$: C, 53.26; H, 3.78; N, 4.78. Found: C, 53.10; H, 3.76; N, 4.64.

*6,6-Dimethyl-2-(4-nitrophenyl)-1,5,7-trioxaspiro[2.5]octane-4,8-dione (**4j**).* This compound was prepared in a manner similar to that described for **4g** from a solution of **3j** (1.38 g, 5.00 mmol) and 35% hydrogen peroxide (3 ml, 35 mmol) in acetonitrile (37 ml): yield 1.10 g (75%); colorless crystals; mp 165-167 °C (from CH_2Cl_2/hexane); ir (KBr) 1794, 1763, 1527 (NO_2) cm^{-1}; ^{1}H nmr (DMSO-d_6) δ 1.78 (3H, s), 1.82 (3H, s), 4.75 (1H, s, 2-CH), 7.75 (2H, ddd, J=1.7, 1.7, and 8.8 Hz, ArH), 8.30 (2H, ddd, J=1.7, 1.7, and 8.8 Hz, ArH); ^{13}C nmr (DMSO-d_6) δ 27.0 (q), 28.1 (q), 58.3 (s, 3-C), 65.4 (d, 2-C), 106.0 (s, 6-C), 123.2 (d, 2C), 129.2 (d, 2C), 137.0 (s), 148.2 (s), 159.8 (s, COO), 162.3 (s, COO). *Anal.* Calcd for $C_{13}H_{11}NO_7$: C, 53.26; H, 3.78; N, 4.78. Found: C, 53.13; H, 3.78; N, 4.87.

*2-(3-Methoxyphenyl)-6,6-dimethyl-1,5,7-trioxaspiro[2.5]octane-4,8-dione (**4k**).* This compound was prepared in a manner similar to that described for **4a** from a solution of **3k** (1.21 g, 4.63 mmol) and 35% hydrogen peroxide (3 ml, 35 mmol) in acetonitrile (17 ml): yield 965 mg (76%); colorless crystals; mp 100-101 °C (from benzene/hexane); ir (KBr) 1798, 1765 cm^{-1}; ^{1}H nmr ($CDCl_3$) δ 1.77 (3H, s), 1.79 (3H, s), 3.84 (3H, s), 4.61 (1H, s, 2-CH), 6.9-7.5 (4H, m, ArH); ^{13}C nmr ($CDCl_3$) δ 27.6 (q), 28.1 (q), 55.4 (q), 58.6 (s, 3-C), 68.4 (d, 2-C), 105.9 (s, 6-C), 112.2 (d), 116.5 (d), 120.0 (d), 129.6 (d), 130.2 (s), 149.2 (s), 159.7 (s, COO), 163.0 (s, COO); LRms m/z (rel. intensity) 278 (M^+; 8), 136 (100). *Anal.* Calcd for $C_{14}H_{14}O_6$: C, 60.43; H, 5.07. Found: C, 60.21; H 5.05.

*6,6-Dimethyl-2-(3-methylphenyl)-1,5,7-trioxaspiro[2.5]octane-4,8-dione (**4l**).* This compound was prepared in a manner similar to that described for **4a** from a solution of **3l** (1.23 g, 5.00 mmol) and 35% hydrogen peroxide (3 ml, 35 mmol) in acetonitrile (17 ml): yield 825 mg (63%); colorless crystals; mp 134-137 °C (from benzene/hexane); ir (KBr) 1800, 1767 cm^{-1}; ^{1}H nmr ($CDCl_3$) δ 1.77 (6H, s), 2.38 (3H, s), 4.60 (1H, s, 2-CH), 7.2-7.5 (4H, m, ArH); ^{13}C nmr ($CDCl_3$) δ 21.2 (q), 27.5 (q), 28.1 (q), 58.7 (s, 3-C), 68.5 (d, 2-C), 105.9 (s, 6-C), 124.9 (d), 128.1 (d), 128.4 (d), 128.8 (s), 131.2 (d), 138.4 (s), 159.6 (s, COO), 163.2 (s, COO); LRms m/z (rel. intensity) 262 (M^+; 5), 120 (100). HRms: Found: m/z 262.0833. Calcd for $C_{14}H_{14}O_5$: M, 262.0841.

*Epoxidation of 1,4-Di(2,2-dimethyl-1,3-dioxane-4,6-dione-5-ene)methylbenzene (**8**) with Hydrogen Peroxide in Acetonitrile.* The acylal (**8**: 1.92 g, 4.98 mmol) was suspended in a mixture of acetonitrile (37 ml) and 35% hydrogen peroxide (3 ml, 35 mmol) and then dissolved at 50 °C for 1 min in a water bath. The solution was stirred at room temperature. After 15 min, colorless crystals were depositing and stirring was continued for 10 min. To the suspension was slowly added 10% $NaHSO_3$ (20 ml) with cooling in an ice bath and then water (30 ml) was added. The precipitates were filtered and washed with cold methanol to give 1,4-di(6,6-dimethyl-1,5,7-trioxa-4,8-dioxospiro[2.5]octane-2-yl)benzene (**9**: 1.04 g, 50%) as colorless crystals: mp 174-177 °C; ir (KBr) 1799, 1759 cm^{-1}; ^1H nmr (DMSO-d_6) δ 1.78 (6H,s), 1.80 (6H, s), 4.65 (2H, s, 2-CH), 7.61 (8H, s, ArH). *Anal.* Calcd for $C_{20}H_{18}O_{10}$: C, 57.42; H, 4.34. Found: C, 57.61; H, 4.32.

Reaction of 2-Methylbenzylidene Meldrum's Acid with Hydrogen Peroxide.

Method A. A solution of 2-methylbenzylidene Meldrum's acid (**3m**: 617 mg, 2.51 mmol) and 35% hydrogen peroxide (1.5 ml, 35 mmol) in acetonitrile (15 ml) was stirred for 1 h at room temperature; **3m** was consumed over 50% based on ^1H nmr analysis. To the reaction mixture was added water (20 ml). The mixture was extracted with CH_2Cl_2 (20 ml × 2). The combined organic fractions were dried over Na_2SO_4 and evaporated *in vacuo* to give a mixture of **3m**, 2-methylbenzaldehyde (**5a**), hydroxy Meldrum's acid (**7**), and 2-(2-methylphenyl)-6,6-dimethyl-1,5,7-trioxaspiro[2.5]octane-4,8-dione (**4m**) in a 52:12:9:27 ratio based on ^1H nmr analysis. The residue was chromatographed on silica gel (50 g) using EtOAc-hexane (2:8, *v/v*) to yield a mixture (43 mg) of **3m** and **4m** in a 4:1 ratio. Further isolation of **4m** by silica gel chromatography was failed. Spectroscopic data of **4m** were identical with those measured from the epoxidation of **3m** with mCPBA.

Method B. A solution of **3m** (1.18 g, 4.80 mmol) and 35% hydrogen peroxide (3 ml, 35 mmol) in acetonitrile (17 ml) was allowed to stand at room temperature for 72 h. To the reaction mixture was added 5% $NaHSO_3$ (40 ml) and the solution was extracted with CH_2Cl_2 (20 ml × 2). The organic fractions were combined, dried over Na_2SO_4, and evaporated *in vacuo*. To the residue was added CCl_4 (5 ml). Insoluble precipitates were filtered and washed with cold CCl_4 (2 ml) to give **7** in 17% (130 mg) yield. This compound **7** was partly recrystallized from EtOAc-hexane, which sublimated at *ca.* 120 °C and melted at 133-135 °C (lit.,[26] 136 °C). The mother liquor of the above filtration, stripped of solvents *in vacuo* gave a mixture (429 mg) of **5a**, 2-methylbenzoic acid (**6a**) in a 3:1 ratio based on ^1H nmr analysis.

Epoxidation of 3m with mCPBA. A solution of mCPBA (171 mg, 1.00 mol) in CH_2Cl_2 (10 ml) was added dropwise to a solution of **3m** (235 mg, 0.96 mmol) in CH_2Cl_2 (20 ml) at -5 °C for 10 min. The mixture was stirred at -5 °C for 1 h, washed with sat. $NaHCO_3$ (30 ml), dried over Na_2SO_4, and evaporated *in vacuo* to give crude crystals, which were recrystallized from ether to give **4m** in 20% (52 mg) yield: mp 106-108 °C; ir (KBr) 1796, 1765 cm^{-1}; ^1H nmr ($CDCl_3$) δ 1.82 (6H, s), 2.42 (3H, s), 4.82 (1H, s, 2-CH), 7.1-7.5 (3H, m, ArH), 7.6-7.8 (1H, m, ArH); ^{13}C nmr ($CDCl_3$) δ 19.2 (q), 28.6 (2C, q), 56.0 (s, 3-C), 67.7 (d, 2-C), 105.8 (s, 6-C), 126.0 (d), 126.9 (s), 128.1 (d, 2C), 130.1 (d), 130.4 (d), 136.7 (s), 159.8 (s, COO), 163.4 (s, COO); LRms *m/z* (rel. intensity) 262 (M^+; 11), 120 (100). HRms: Found: *m/z* 262.0879. Calcd for $C_{14}H_{14}O_5$: M, 262.0841.

Reaction of 4-Methylbenzylidene Meldrum's Acid with Hydrogen Peroxide.

Method A. A suspension of 4-methylbenzylidene Meldrum's acid (**3n**: 579 mg, 2.36 mmol) in acetonitrile (15 ml) was dissolved at 50 °C for 5 min. To the solution was added 35% hydrogen peroxide (1.5 ml, 18 mmol) and the mixture was stirred at room temperature for 1 h; **3n** was consumed over 50% based on ^1H nmr analysis. To the reaction mixture was added water (30 ml) and the solution was extracted with CH_2Cl_2 (30 ml × 2). The combined organic fractions were washed with 5% $NaHSO_3$ (40 ml), dried over Na_2SO_4, and evaporated *in vacuo* to afford a mixture of **3n**, 4-methylbenzaldehyde (**5b**), **7**, and 2-(4-methylphenyl)-6,6-dimethyl-1,5,7-trioxaspiro[2.5]octane-4,8-dione (**4n**) in a 18:20:11:25 ratio based on ^1H nmr analysis. The residue was immediately chromatographed on silica gel (50 g). The elution with 20% EtOAc-hexane afforded a mixture (137 mg) of **5b**, **4n**, and **7** in a 66:24:10 ratio based on ^1H nmr analysis. The mixture was dissolved in ether (30 ml) and slowly evaporation of the solvent gave **4n** (42 mg, 13%): colorless crystals; mp 104 -105 °C; ir (KBr) 1793, 1762 cm^{-1}; ^1H nmr ($CDCl_3$) δ 1.75 (3H, s), 1.77 (3H, s), 2.37 (3H, s), 4.61 (1H, s, 2-CH), 7.21 (2H, d, J=8.4 Hz, ArH), 7.43 (2H, d, J=8.4 Hz, ArH); ^{13}C nmr ($CDCl_3$) δ 21.4 (q), 27.7 (q), 28.1 (q), 58.7 (s, 3-C), 68.7 (d, 2-C), 105.8 (s, 6-C), 125.8 (s), 127.4 (d, 2C), 129.3 (d, 2C), 140.7 (s), 159.6 (s, COO), 163.1 (s, COO); LRms *m/z* (rel. intensity) 262 (M^+; 10), 120 (100). HRms: Found: *m/z* 262.0885. Calcd for $C_{14}H_{14}O_5$: M, 262.0841.

Method B. A suspension of **3n** (1.15 g, 4.71 mmol) in acetonitrile (17 ml) was dissolved at 50 °C for 5 min. To the solution was added 35% hydrogen peroxide (3 ml, 35 mmol) and then allowed to stand at room temperature for 72 h. To the reaction mixture was added 5% $NaHSO_3$ (40 ml) and the solution was extracted with CH_2Cl_2 (20 ml × 2). The organic fractions were combined, dried over Na_2SO_4, and evaporated *in vacuo*. To the residue was added CCl_4 (5 ml). Insoluble precipitates were filtered and washed with cold CCl_4 (2 ml) to give **7** in 24% (195 mg) yield. The mother liquor of the above filtration, stripped of solvents *in vacuo* gave a mixture (376 mg) of **5b**, 4-methylbenzoic acid (**6b**), and **7** in a 1:1:0.3 ratio based on ^1H nmr analysis.

Epoxidation of 3n with mCPBA. A solution of mCPBA (177 mg, 1.03 mol) in CH_2Cl_2 (10 ml) was added dropwise to a solution of **3n** (233 mg, 0.95 mmol) in CH_2Cl_2 (20 ml) at -5 °C for 10 min. The mixture was stirred at -5 °C for 1 h, washed with sat. $NaHCO_3$ (30 ml), dried over Na_2SO_4, and evaporated *in vacuo* to give crude crystals, which were recrystallized from ether to give **4n** in 44% (110 mg) yield.

Reaction of 2-Methoxybenzylidene Meldrum's Acid with Hydrogen Peroxide.

Method A. A solution of 2-methoxybenzylidene Meldrum's acid (**3o**: 664 mg, 2.53 mmol) and 35% hydrogen peroxide (1.0 ml, 8 mmol) in acetonitrile (10 ml) was stirred at room temperature for 90 min; **3o** was consumed over 50% based on ^1H nmr analysis. To the reaction mixture was added water (30 ml). The mixture was extracted with CH_2Cl_2 (20 ml × 2) and the combined organic fractions were washed with 5% $NaHSO_3$ (20 ml), dried over Na_2SO_4, and evaporated *in vacuo* to give a mixture of **3o**, 2-methoxybenzaldehyde (**5c**), **7**, and 2-(2-methoxyphenyl)-6,6-dimethyl-1,5,7-trioxaspiro[2.5]octane-4,8-dione (**4o**) in a 50:17:12:21 ratio based on ^1H nmr analysis. The mixture was dissolved in ether (3 ml) and slowly evaporation of the solvent gave **4o** in 4% (14 mg) yield: colorless crystals; mp 88-90 °C; ir (KBr) 1793, 1764 cm^{-1}; ^1H nmr ($CDCl_3$) δ 1.78 (3H, s), 1.88 (3H, s), 3.82 (3H, s), 4.92 (1H, s, 2-CH), 6.88 (1H, d, J=8.0 Hz, ArH), 7.07 (1H, dd, J=7.6 and 7.6 Hz, ArH), 7.39 (1H, ddd, J=2.2, 8.0, 8.0 Hz, ArH), 7.60 (1H, dd, J=2.2 and 7.6 Hz, ArH); LRms *m/z* (rel. intensity) 278 (M^+; 36), 136 (100). HRms: Found: *m/z* 278.0762. Calcd for $C_{14}H_{14}O_6$: M, 278.0790.

Method B. A solution of **3o** (1.25 g, 5.0 mmol) and 35% hydrogen peroxide (3 ml, 35 mmol) in acetonitrile (17 ml) was allowed to stand for 72 h and then added with water 50 ml. The mixture was extracted with CH_2Cl_2 (50 ml × 2) and the combined organic layers were washed with 5% $NaHSO_3$ (40 ml), dried over Na_2SO_4, and evaporated *in vacuo*. To the residue was added CCl_4 (4 ml). Insoluble precipitates were filtered and washed with cold CCl_4 (2 ml) to give **7** in 1.6% (13 mg) yield. The mother liquor of the above filtration, stripped of solvents *in vacuo* gave a mixture (166 mg) of **5c** and 2-methoxybenzoic acid (**6c**) in a 47:10 ratio based on ^1H nmr analysis.

Reaction of 4-Methoxybenzylidene Meldrum's Acid with Hydrogen Peroxide. A solution of 4-methoxybenzylidene Meldrum's acid (**3p**: 658 mg, 2.51 mmol) and 35% hydrogen peroxide (3 ml, 35 mmol) in acetonitrile (17 ml) was allowed to stand for 72 h and then added with water 30 ml. The mixture was extracted with CH_2Cl_2 (50 ml × 2) and the combined organic layers were washed with 5% $NaHSO_3$ (40 ml), dried over Na_2SO_4, and evaporated *in vacuo*. To the residue was added CCl_4 (4 ml). Insoluble precipitates were filtered and washed with cold CCl_4 (2 ml) to give a mixture (35 mg) of **7** and 4-methoxybenzoic acid (**6d**) in a 1:2 ratio based on ^1H nmr analysis. The mother liquor of the above filtration, stripped of solvents *in vacuo* gave a mixture (111 mg) of 4-methoxybenzaldehyde (**5d**) and **6d** in a 16:1 ratio based on ^1H nmr analysis.

*Reaction of **3m-p** with Hydrogen Peroxide in Acetonitrile-d3.* To an acetonitrile-d_3 solution (0.4 ml) of **3m-p** (*ca.* 10 mg) in an nmr tube was added 35% hydrogen peroxide (0.05 ml, 0.06 mmol). The progress of the reaction was monitored by ^1H nmr.

Epoxidation of Chiral 4-Nitrobenzylidene Spirocyclic Acylal.

Method A. To a solution of the mixture of chiral (*E*)- and (*Z*)-4-nitrobenzylidene spirocyclic acylals (**11a-*Z*** and **11a-*E***: *ca.* 1:1 ratio; 1.00 g, 2.69 mmol) in acetonitrile (70 ml) at room temperature, 35% hydrogen peroxide (10 ml, 0.118 mol) was added slowly dropwise and stirred continuously for 40 min. A half volume of solvent was evaporated *in vacuo* below 40 °C. To the reaction mixture was added CH_2Cl_2 (20 ml) and the organic layer was separated. The aqueous layer was further extracted with CH_2Cl_2 (20 ml). The combined organic layers were washed with 10% $NaHSO_3$ (100 ml), dried ($MgSO_4$), and evaporated *in vacuo* to give a mixture of (2*S*,3*S*,6*S*,7*S*,10*R*)-7-isopropyl-10-methyl-2-(4-nitrophenyl)-1,5,12-trioxadispiro[2.2.5.2]tridecane-4,13-dione (**12a-*S***) and (2*R*,3*S*,6*R*,7*S*,10*R*)-7-isopropyl-10-methyl-2-(4-nitrophenyl)-1,5,12-trioxadispiro[2.2.5.2]tridecane-4,13-dione (**12a-*R***) whose ratio was measured as *ca.* **12a-*S***:**12a-*R***=1:1 by ^1H nmr analysis. The epoxides were isolated by silica gel column chromatography (100 g) using hexane/EtOAc (13:87, *v/v*) as an eluent. The first elution afforded **12a-*R*** (158 mg, 15%): colorless crystals; mp 189-191 °C (from ether); $[\alpha]_D^{12}$ +155° (*c* 1.03, acetone); ir (KBr) 1795, 1764, 1528 (NO_2) cm^{-1}; ^1H nmr ($CDCl_3$) δ 0.94 (3H, d, *J*=7.0 Hz, isopropyl Me), 0.97 (3H, d, *J*=7.0 Hz, isopropyl Me), 0.98 (3H, d, *J*=5.3 Hz, 10-Me), 1.1-2.1 (8H, m), 2.27 (1H, m, isopropyl CH), 4.75 (1H, s, 2-CH), 7.75 (2H, ddd, *J*=2.0, 2.0, and 8.8 Hz, ArH), 8.29 (2H, ddd, *J*=2.0, 2.0, and 8.8 Hz, ArH); ^{13}C nmr ($CDCl_3$) δ 18.3 (q), 21.7 (q), 21.9 (q), 23.3 (q), 25.0 (d), 29.6 (d), 33.4 (t), 47.6 (t), 49.3 (d), 61.8 (s, 3-C), 66.5 (d, 2-C), 109.5 (s, 6-C), 123.7 (d, 2C), 128.8 (d, 2C), 135.7 (s), 149.0 (s), 159.7 (s, COO), 162.4 (s, COO). *Anal.* Calcd for $C_{20}H_{23}NO_7$: C, 61.68; H, 5.95; N, 3.60. Found: C, 61.59;

H, 5.95; N, 3.51. The next elution afforded **12a-*S*** (179 mg, 17%): colorless crystals; mp 182-185 °C (from ether); $[\alpha]_D^{13}$ -91° (*c* 1.04, acetone); ir (KBr) 1800, 1764, 1522 (NO_2) cm^{-1}; ^{1}H nmr ($CDCl_3$) δ 0.83 (3H, d, *J*=5.7 Hz, 10-Me), 0.97 (3H, d, *J*=7.1 Hz, isopropyl Me), 0.98 (3H, d, *J*=7.1 Hz, isopropyl Me), 1.0-2.1 (8H, m), 2.25 (1H, m, isopropyl CH), 4.75 (1H, s, 2-CH), 7.74 (2H, ddd, *J*=2.0, 2.0, and 8.8 Hz, ArH), 8.30 (2H, ddd, *J*=2.0, 2.0, and 8.8 Hz, ArH); ^{13}C nmr ($CDCl_3$) δ 18.3 (q), 21.5 (q), 21.9 (q), 23.3 (q), 25.0 (d), 29.4 (d), 33.2 (t), 47.7 (t), 49.3 (d), 58.0 (s, 3-C), 66.4 (d, 2-C), 109.5 (s, 6-C), 123.6 (d, 2C), 128.7 (d, 2C), 135.8 (s), 149.1 (s), 159.1 (s, COO), 162.9 (s, COO). *Anal.* Calcd for $C_{20}H_{23}NO_7$: C, 61.68; H, 5.95; N, 3.60. Found: C, 61.50; H, 5.96; N, 3.59. The ^{1}H nmr spectra of **12a-*S*** and **12a-*R*** using the chiral shift regent showed the absence of a chiral isomer.

Method B. The chiral acylal (**11a-*Z***: 177 mg, 0.47 mmol) was dissolved in EtOAc (10 ml) at -20 °C and then cooled to -78 °C. Na_2CO_3 (61 mg, 0.58 mmol) was added to the cooling solution. The temperature of the solution was maintained at -78 °C and a solution of mCPBA (91 mg, 0.53 mmol) in CH_2Cl_2 (20 ml) was slowly added dropwise for 10 min to the solution of **11a-*Z*** and further stirred for 1 h. The reaction mixture was allowed to slowly warm to room temperature and was then washed with 10% $NaHSO_3$ (20 ml). The aqueous layer was extracted with CH_2Cl_2 (20 ml × 2). The organic fractions were combined, washed with sat. $NaHCO_3$ (100 ml), dried ($MgSO_4$), and evaporated *in vacuo*. The residue crystals were slowly recrystallized from ether to give **12a-*S*** (170 mg, 92%).

Epoxidation of Chiral 4-Chlorobenzylidene Spirocyclic Acylal.

Method A. In a manner similar to that described for the preparation in Method A, the epoxidation of a mixture of chiral (*E*)- and (*Z*)-4-chlorobenzylidene spirocyclic acylals (**11b-*E*** and **11b-*Z***: *ca.* 1:1 ratio; 1.00 g, 2.76 mmol) with 35% hydrogen peroxide (10 ml, 0.118 mol) in acetonitrile (50 ml) gave (2*R*,3*S*,6*R*,7*S*,10*R*)-2-(4-chlorophenyl)-7-isopropyl-10-methyl-1,5,12-trioxadispiro[2.2.5.2]tridecane-4,13-dione (**12b-*R***: 289 mg, 28%) from the first elution and (2*S*,3*S*,6*S*,7*S*,10*R*)-2-(4-chlorophenyl)-7-isopropyl-10-methyl-1,5,12-trioxadispiro-[2.2.5.2]tridecane-4,13-dione (**12b-*S***: 290 mg, 28%) from the second elution.

12b-*R*: Colorless crystals; mp 131-134 °C (from ether); $[\alpha]_D^{21}$ +150° (*c* 1.54, acetone); ir (KBr) 1800, 1761 cm^{-1}; ^{1}H nmr ($CDCl_3$) δ 0.93 (3H, d, *J*=7.0 Hz, 10-Me), 0.96 (6H, d, *J*=6.7 Hz, isopropyl Me), 1.0-2.1 (8H, m), 2.27 (1H, m, isopropyl CH), 4.61 (1H, s, 2-CH), 7.3-7.6 (4H, m, ArH); ^{13}C nmr ($CDCl_3$) δ 18.3 (q), 21.5 (q), 21.9 (t), 23.3 (q), 24.9 (d), 29.5 (d), 33.4 (t), 47.2 (t), 49.3 (d), 58.4 (s, 3-C), 67.6 (d, 2-C), 109.2 (s, 6-C), 127.4 (s), 128.8 (2C, d), 129.0 (2C, d), 136.4 (s), 160.0 (s, COO), 162.8 (s, COO). *Anal.* Calcd for $C_{20}H_{23}O_5Cl$: C, 63.41; H, 6.12. Found: C 63.29; H, 6.03.

12b-*S*: Colorless crystals; mp 133-136 °C (from ether); $[\alpha]_D^{12}$ -87° (*c* 0.51, acetone); ir (KBr) 1797, 1763 cm^{-1}; ^{1}H nmr ($CDCl_3$) δ 0.81 (3H, d, *J* =5.8 Hz, 10-Me), 0.90 (3H, d, *J*=7.1 Hz, isopropyl Me), 0.98 (3H, d, *J*=7.1 Hz, isopropyl Me), 1.1-2.2 (8H, m), 4.60 (1H, s, 2-CH), 7.3-7.6 (4H, m, ArH) ^{13}C nmr ($CDCl_3$) δ 18.3 (q), 21.3 (q), 21.9 (t), 23.3 (q), 25.0 (d), 29.4 (d), 33.3 (t), 47.4 (t), 49.3 (d), 58.5 (s, 3-C), 67.5 (d, 2-C), 109.2 (s, 6-C), 127.3 (s), 128.8 (2C, d), 128.9 (2C, d), 136.6 (s), 159.3 (s, COO), 163.3 (s, COO). *Anal.* Calcd for $C_{20}H_{23}O_5Cl$: C, 63.41; H, 6.12. Found: C, 63.39; H, 6.02.

Method B. In a manner similar to that described for the preparation in Method B, the epoxidation of **11b**-***E*** (262 mg, 0.72 mmol) with mCPBA (141 mg, 0.82 mmol) gave **12b**-***R*** in 71% (192 mg) yield.

X-Ray Structure Analyses. All crystals used for the X-ray measurements were grown from ether solutions. All measurements were made on an MAC Science MXC18 diffractometer with graphite monochromated Cu-*Kα* radiation (λ=1.54178 Å).

Table 5. Atomic Coordinates and Equivalent Isotropic Thermal Parameters of Non-Hydrogen Atoms of **12a**-*S*

Atom	*x*	*y*	*z*	B_{eq}/Å^2	Atom	*x*	*y*	*z*	B_{eq}/Å^2
O(1)	-0.3644(8)	-0.1069(6)	-0.0621(4)	4.31(9)	O(2)	-0.0741(9)	-0.2178(6)	0.0981(4)	5.3(1)
O(3)	-0.0277(8)	0.0205(6)	0.2412(4)	3.34(8)	O(4)	-0.2813	0.2009	0.2205	3.00(7)
O(5)	-0.5629(8)	0.1328(7)	0.0591(4)	4.86(10)	O(6)	0.003(1)	0.7886(8)	-0.2478(5)	8.0(2)
O(7)	-0.389(1)	0.6431(8)	-0.3165(6)	9.4(2)	N(1)	-0.192(1)	-0.6576(9)	-0.2613(5)	6.1(2)
C(1)	-0.146(1)	0.0476(8)	-0.0551(5)	3.6(1)	C(2)	-0.2447(10)	0.0079(7)	0.0513(5)	3.2(1)
C(3)	-0.1086(10)	-0.0752(8)	0.1297(5)	3.5(1)	C(4)	-0.395(9)	0.2068(7)	0.2718(5)	2.9(1)
C(5)	-0.3751(10)	0.1213(8)	0.1079(5)	3.2(1)	C(6)	-0.0007(10)	0.2595(8)	0.4032(5)	3.4(1)
C(7)	0.011(1)	0.4607(8)	0.4418(5)	4.6(1)	C(8)	0.211(1)	0.6001(8)	0.3985(6)	5.5(2)
C(9)	0.177(1)	0.5478(8)	0.2679(5)	4.2(1)	C(10)	0.162(1)	0.3461(8)	0.2281(5)	3.4(1)
C(11)	-0.1679(10)	0.2057(8)	-0.1093(5)	3.5(1)	C(12)	0.049(1)	0.3584(9)	-0.0980(5)	4.0(1)
C(13)	0.042(1)	0.5076(8)	-0.1464(5)	4.7(1)	C(14)	-0.180(1)	0.5005(9)	-0.2048(5)	4.3(1)
C(15)	-0.396(1)	0.3515(10)	-0.2176(5)	4.9(2)	C(16)	-0.389(1)	0.2032(8)	-0.1675(5)	4.4(1)
C(17)	0.385(1)	0.6775(9)	0.2232(6)	6.0(2)	C(18)	-0.182(1)	0.1150(8)	0.4560(5)	3.6(1)
C(19)	-0.053(1)	0.115(1)	0.5769(6)	5.8(2)	C(20)	-0.422(1)	0.1452(9)	0.4615(6)	5.0(1)

Table 6. Selected Bond Lengths (*l*/Å) and Angles (*Φ*/°) of **12a**-*S*

O(1)-C(1)	1.422(6)	O(1)-C(2)	1.424(5)	O(2)-C(3)	1.198(5)	O(3)-C(3)	1.341(5)
O(3)-C(4)	1.455(5)	O(4)-C(4)	1.444(5)	O(4)-C(5)	1.330(5)	O(5)-C(5)	1.206(5)
O(6)-N(1)	1.223(7)	O(7)-N(1)	1.207(7)	N(1)-C(14)	1.498(7)	C(1)-C(2)	1.506(6)
C(1)-C(11)	1.504(7)	C(2)-C(3)	1.494(6)	C(2)-C(5)	1.488(6)	C(4)-C(6)	1.513(6)
C(4)-C(10)	1.539(6)	C(6)-C(7)	1.525(7)	C(6)-C(18)	1.561(7)	C(7)-C(8)	1.532(8)
C(8)-C(9)	1.507(7)	C(9)-C(10)	1.525(7)	C(9)-C(17)	1.537(7)	C(18)-C(19)	1.523(7)
C(18)-C(19)	1.512(7)						

C(1)-O(1)-C(2)	63.9(3)	C(3)-O(3)-C(4)	118.9(3)	C(4)-O(4)-C(5)	119.0(3)
O(6)-N(1)-O(7)	126.1(6)	O(6)-N(1)-C(14)	116.3(6)	O(7)-N(1)-C(14)	117.6(6)
O(1)-C(1)-C(2)	58.1(3)	O(1)-C(1)-C(11)	118.4(4)	C(2)-C(1)-C(11)	122.5(4)
O(1)-C(2)-C(1)	58.0(3)	O(1)-C(2)-C(3)	115.9(4)	O(1)-C(2)-C(5)	117.1(4)
C(1)-C(2)-C(3)	115.5(4)	C(1)-C(2)-C(5)	121.6(4)	C(3)-C(2)-C(5)	116.1(4)
O(2)-C(3)-O(3)	121.0(4)	O(2)-C(3)-C(2)	123.9(5)	O(3)-C(3)-C(2)	115.1(4)
O(3)-C(4)-O(4)	109.3(3)	O(3)-C(4)-C(6)	107.3(3)	O(3)-C(4)-C(10)	109.3(4)
O(4)-C(4)-C(6)	108.7(3)	O(4)-C(4)-C(10)	111.1(3)	C(6)-C(4)-C(10)	111.1(4)
O(4)-C(5)-O(5)	120.7(4)	O(4)-C(5)-C(2)	115.6(4)	O(5)-C(5)-C(2)	123.5(4)
C(4)-C(6)-C(7)	109.9(4)	C(4)-C(6)-C(18)	114.5(4)	C(7)-C(6)-C(18)	114.1(4)
C(6)-C(7)-C(8)	112.1(4)	C(7)-C(8)-C(9)	111.5(4)	C(8)-C(9)-C(10)	110.7(4)
C(8)-C(9)-C(17)	112.5(5)	C(10)-C(9)-C(17)	108.6(5)	C(4)-C(10)-C(9)	112.0(4)
C(1)-C(11)-C(12)	120.6(5)	C(1)-C(11)-C(16)	122.4(5)	N(1)-C(14)-C(13)	119.4(6)
N(1)-C(14)-C(15)	117.6(5)	C(6)-C(18)-C(19)	109.4(4)	C(6)-C(18)-C(20)	114.6(4)
C(19)-C(18)-C(20)	110.2(5)				

12a-S: A crystal of $C_{20}H_{23}NO_7$ having approximate dimensions of 0.40 x 0.40 x 0.30 mm was mounted on a glass fiber. Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 22 carefully centered reflections in the range $5.00<2\theta<60.00°$ corresponded to a triclinic cell with dimensions: a=5.882(3) Å, b=7.740(3) Å, c=11.901(4) Å, α=99.35(3)°, β=98.59(3)°, 109.01(3), V=493.5(4) Å^3. For Z=1 and F.W.=389.40, the calculated density is 1.31 g cm^{-3}. Based on a statistical analysis of intensity distribution, and the successful solution and refinement of the structure, the space group was determined to be $P1$. The data were collected at a temperature of 22±1 °C using the ω-2θ scan technique to a maximum 2θ value of 126.6°. Omega scans of several intense reflections, made prior to data collection, had an average width at half-height of 0.63°. Scans of (2.82+0.2 tanθ)° were made at speed of 14° min^{-1} (in omega). The weak reflections [F<7.0δ(F)] were rescanned (maximum of 3 scans) and the counts were accumulated to ensure good counting statistics. Of the 1746 reflections which were collected, 1610 were unique (R_{int}=0.079). The intensities of three representative reflections were measured after every 100 reflections. No decay correction was applied. The linear absorption coefficient, μ, for Cu-$K\alpha$ radiation was 8.4 cm^{-1}. The data were corrected for Lorentz and polarization effects. A correction for secondary extinction was applied (coefficient=3.44119e-0.5). The structure was solved by direct methods (SAPI91)[27] and expanded using Fourier techniques (DIRDIF92).[28] The non-hydrogen atoms were anisotropically refined. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on 1565 observed reflections [I>3.00δ(I)] and 251 variable parameters and converged (largest parameter was 0.00 times its esd) with unweighted and weighted agreement factors of R=0.047 and R_ω=0.047. The standard deviation of an observation of unit weight was 6.53. The weighting scheme was based on counting statistics and included a factor (p=0.005) to downweight the intense reflections. Plots of $\Sigma\omega(|F_o| - |F_c|)^2$ vs. $|F_o|$, reflections order in data collection, sinθ/λ and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.19 and -0.22e$^-$/Å^3, respectively. Neutral atom scattering factors were taken from Cromer and Waber.[29] Anomalous dispersion effects were included in Fcalc;[30] the values for Δf' and Δf" were those of Creagh and McAuley.[30] The values for the mass attenuation coefficients are those of Creagh and Hubbel.[31] All calculations were performed using the TEXSAN[32] crystallographic software package of Molecular Structure Corporation. The atomic coordinates are listed in Table 5 and selected bond lengths and angles in Table 6.

Table 7. Atomic Coordinates and Equivalent Isotropic Thermal Parameters of Non-Hydrogen Atoms of **12a-*R***

Atom	x	y	z	B_{eq}/Å^2	Atom	x	y	z	B_{eq}/Å^2
O(1)	-0.4438(2)	-0.1977(1)	-0.7874(2)	4.19(5)	O(2)	-0.2052(2)	-0.2139(1)	-0.8895(2)	4.33(5)
O(3)	-0.2604(2)	-0.1723(1)	-1.0866(2)	3.31(4)	O(4)	-0.4532(2)	-0.1137(1)	-1.1180(2)	3.38(4)
O(5)	-0.5908(2)	-0.1101(1)	-0.9570(2)	5.10(6)	O(6)	-0.2753(3)	-0.5966(1)	-0.8935(3)	7.83(8)
O(7)	-0.1594(3)	-0.5526(2)	-0.7387(3)	7.25(8)	N(1)	-0.2426(3)	-0.5458(2)	-0.8187(3)	5.41(8)
C(1)	-0.4797(3)	-0.2598(2)	-0.8675(3)	3.53(7)	C(2)	-0.4187(3)	-0.1912(2)	-0.9255(3)	3.06(6)
C(3)	-0.2868(3)	-0.1948(1)	-0.9619(3)	3.09(6)	C(4)	-0.3567(3)	-0.1558(2)	-1.1810(3)	2.98(6)
C(5)	-0.4983(3)	-0.1357(2)	-0.9988(3)	3.42(7)	C(6)	-0.2977(3)	-0.1048(2)	1.2856(3)	3.26(6)
C(7)	-0.3888(3)	-0.0906(2)	-1.3971(3)	4.18(7)	C(8)	-0.4343(3)	-0.1641(2)	-1.4584(3)	4.61(8)
C(9)	-0.4944(3)	-0.2154(2)	-1.3540(3)	4.17(7)	C(10)	-0.4065(3)	-0.2286(2)	-1.2396(3)	3.69(7)
C(11)	-0.4175(3)	-0.3336(2)	-0.8513(3)	3.57(7)	C(12)	-0.4429(3)	-0.3909(2)	0.9414(3)	4.10(7)
C(13)	-0.3865(3)	-0.4606(2)	-0.9302(3)	4.38(8)	C(14)	-0.3052(3)	-0.4722(2)	-0.8289(3)	4.05(7)
C(15)	-0.2796(3)	-0.4174(2)	-0.7356(3)	4.62(8)	C(16)	-0.3365(3)	-0.3473(2)	-0.7489(3)	4.41(8)
C(17)	-0.5370(4)	-0.2897(2)	-1.4144(4)	6.7(1)	C(18)	-0.2376(3)	-0.0319(2)	-1.2295(3)	4.18(7)
C(19)	-0.1310(3)	-0.0082(2)	-1.3169(4)	5.75(9)	C(20)	-0.3237(4)	-0.0349(2)	-1.2118(5)	6.2(1)

Table 8. Selected Bond Lengths (l/Å) and Angles (Φ/°) of **12a-*R***

O(1)-C(1)	1.416(3)	O(1)-C(2)	1.423(3)	O(2)-C(3)	1.119(3)	O(3)-C(3)	1.349(3)
O(3)-C(4)	1.446(3)	O(4)-C(4)	1.437(3)	O(4)-C(5)	1.355(3)	O(5)-C(5)	1.183(3)
O(6)-N(1)	1.225(4)	O(7)-N(1)	1.220(4)	N(1)-C(14)	1.471(4)	C(1)-C(2)	1.499(4)
C(1)-C(11)	1.477(4)	C(2)-C(3)	1.485(4)	C(2)-C(5)	1.503(4)	C(4)-C(6)	1.529(4)
C(4)-C(10)	1.515(4)	C(6)-C(7)	1.520(4)	C(6)-C(18)	1.550(4)	C(7)-C(8)	1.521(4)
C(8)-C(9)	1.535(4)	C(9)-C(10)	1.516(4)	C(9)-C(17)	1.519(4)	C(18)-C(19)	1.516(4)
C(18)-C(20)	1.518(4)						
C(1)-O(1)-C(2)	63.7(2)	C(3)-O(3)-C(4)	121.2(2)	C(4)-O(4)-C(5)	120.5(2)		
O(6)-N(1)-O(7)	123.5(2)	O(6)-N(1)-C(14)	118.6(3)	O(7)-N(1)-C(14)	118.0(3)		
O(1)-C(1)-C(2)	58.4(2)	O(1)-C(1)-C(11)	119.5(2)	C(2)-C(1)-C(11)	123.4(2)		
O(1)-C(2)-C(1)	57.9(2)	O(1)-C(2)-C(3)	115.1(2)	O(1)-C(2)-C(5)	115.0(2)		
C(1)-C(2)-C(3)	119.4(3)	C(1)-C(2)-C(5)	117.5(2)	C(3)-C(2)-C(5)	117.7(2)		
O(2)-C(3)-O(3)	119.5(3)	O(2)-C(3)-C(2)	125.4(2)	O(3)-C(3)-C(2)	115.1(2)		
O(3)-C(4)-O(4)	110.2(3)	O(3)-C(4)-C(6)	105.5(3)	O(3)-C(4)-C(10)	110.2(3)		
O(4)-C(4)-C(6)	107.9(2)	O(4)-C(4)-C(10)	110.4(2)	C(6)-C(4)-C(10)	112.4(2)		
O(4)-C(5)-O(5)	121.0(3)	O(4)-C(5)-C(2)	114.4(2)	O(5)-C(5)-C(2)	124.5(3)		
C(4)-C(6)-C(7)	109.5(2)	C(4)-C(6)-C(18)	114.5(2)	C(7)-C(6)-C(18)	114.1(2)		
C(6)-C(7)-C(8)	111.9(3)	C(7)-C(8)-C(9)	111.3(3)	C(8)-C(9)-C(10)	110.0(2)		
C(8)-C(9)-C(17)	111.4(3)	C(10)-C(9)-C(17)	111.4(5)	C(4)-C(10)-C(9)	113.1(3)		
C(1)-C(11)-C(12)	118.7(3)	C(1)-C(11)-C(16)	122.1(3)	N(1)-C(14)-C(13)	119.0(3)		
N(1)-C(14)-C(15)	118.6(3)	C(6)-C(18)-C(19)	110.0(3)	C(6)-C(18)-C(20)	115.2(3)		
C(19)-C(18)-C(20)	109.1(3)						

12a-R: A crystal of $C_{20}H_{23}NO_7$ having approximate dimensions of 0.50 x 0.50 x 0.40 mm was mounted on a glass fiber. Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 22 carefully centered reflections in the range $5.00<2\theta<60.00°$ corresponded to a orthorhombic cell with dimensions: a=10.896(2) Å, b=17.652(4) Å, c=10.081(2) Å, V=1939.1(6) Å^3. For Z=4 and F.W.=389.40, the calculated density is 1.33 g cm^{-3}. The systematic absence of $h00$: $h\neq2n$, $0k0$: $k\neq2n$, $00l$: $l\neq2n$, uniquely determine the space group to be $P2_1P2_1P2_1$. The data were collected at a temperature of 22±1 °C using the ω-2θ scan technique to a maximum 2θ value of 128.5°. Omega scans of several intense reflections, made prior to data collection, had an average width at half-height of 0.22°. Scans of $(1.01+0.2\tan\theta)°$ were made at speed of 14° min^{-1} (in omega). The weak reflections $|F<7.0\sigma(F)|$ were rescanned (maximum of 3 scans) and the counts were accumulated to ensure good counting statistics. A total of 1884 reflections was collected. The intensities of three representative reflections were measured after every 100 reflections. No decay correction was applied. The linear absorption coefficient, μ, for Cu-$K\alpha$ radiation was 8.5 cm^{-1}. The data were corrected for Lorentz and polarization effects. A correction for secondary extinction was applied (coefficient=1.79519e-0.5). The structure was solved by direct methods (MITHRIL84)[33] and expanded using Fourier techniques (DIRDIF92).[28] The non-hydrogen atoms were anisotropically refined. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on 1786 observed reflections $[I>3.00\sigma(I)]$ and 254 variable parameters and converged (largest parameter was 0.01 times its esd) with unweighted and weighted agreement factors of R=0.036 and R_ω=0.036. The standard deviation of an observation of unit weight was 4.19. The weighting scheme was based on counting statistics and included a factor (p=0.007) to downweight the intense reflections. Plots of $\Sigma\omega(|F_o| - |F_c|)^2$ vs. $|F_o|$, reflections order in data collection, $\sin\theta/\lambda$ and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.15 and -0.16e$^-$/Å^3, respectively. Neutral atom scattering factors, anomalous dispersion effects, the values for the mass attenuation coefficients, and all calculations were were worked up in a similar manner previously mentioned. The atomic coordinates are listed in Table 7 and selected bond lengths and angles in Table 8

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