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Stereoselective Isomerizations of 4-(2′-Chloro-3′-methoxyphenyl)-2,5-dimethyl-1,3-dioxolanes: Stereochemistry and Conformation of the Product 2-Benzopyrans

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Stereoselective isomerization of *rel*-(2*R*,4*S*,5*R*)-4-(2′-chloro-3′-methoxyphenyl)-2,5-dimethyl-1,3-dioxolane **5** with titanium(IV) chloride afforded solely *rel*-(1*R*,3*R*,4*S*)-5-chloro-4-hydroxy-6-methoxy-1,3-dimethyl-2-benzopyran **17** in high yield in which the conformation adopted by the dihydropyran ring minimized *peri*-interactions through stereochemistries that were axial for the C-3 methyl, pseudoaxial for the C-4 hydroxy and pseudoequatorial for the C-1 methyl groups. Similar isomerization of the individual *rel*-(2*S*,4*R*,5*R*)- and *rel*-(2*R*,4*R*,5*R*)-diastereoisomeric dioxolanes **6** and **7** gave solely the corresponding *rel*-(1*S*,3*R*,4*R*)-2-benzopyran **25** in which the orientations of the substituents at C-3, C-4 and C-1 were equatorial, pseudoaxial and pseudoequatorial respectively. These observations differed significantly from those previously made for the related isomerizations of the corresponding 4-(2′-chloro-5′-methoxyphenyl)-2,5-dimethyl-1,3-dioxolanes.

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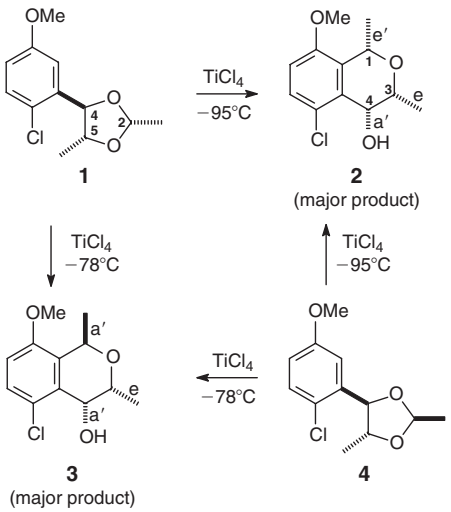
Introduction

In connection with our search[1] for convenient routes to naturally occurring naphthopyrans and their quinones,[2,3] we have shown previously that 4-aryl-2,5-dimethyl-1,3-dioxolanes are readily isomerized to 4-hydroxy-1,3-dimethyl-2-benzopyrans using titanium(IV) chloride. In these rearrangements, which may be undertaken for either the racemates[4,5] or the enantiopure compounds,[6] the *vicinal* stereochemistries at C-4 and C-5 of the dioxolanes are transferred unaltered to C-4 and C-3, respectively, of the 2-benzopyrans. The third stereogenic centre, C-1 of the 2-benzopyrans, is derived from C-2 of the parent dioxolanes,[5] but here the stereochemistry is not transferred from substrates to products. Furthermore, the configuration at this C-1 centre can be reversed dramatically by varying, over a small range, the temperature at which the transformation is undertaken. In particular, for the conversions of the C-2 epimeric 4-(2′-chloro-5′-methoxyphenyl)-2,5-dimethyl-1,3-dioxolanes **1** and **4** (Scheme 1), each gave the pseudoequatorial C-1 methyl-2-benzopyran **2** as the major (28:1) product at −95°C, while at −78°C the major (~3:1) product was the pseudoaxial C-1 epimer **3**.[5] The factors that determine the derived orientation at C-1 are not well understood. It is possible that in this case this dramatic change is promoted by steric compression arising through the greater *peri*-interactions between the pseudoequatorial C-1 methyl and C-8 methoxy groups in product **2** relative to those in **3**, where the C-1 methyl is pseudoaxial. In order to explore this possibility the three dioxolanes **5**, **6** and **7** were assembled. Thus the sole change for the latter two compounds from the substrates **1** and **4** investigated in the previous study[5] involved the transfer of the activating methoxy substituent from being *ortho*- to being *para*- to the site of ring-closure in the isomerization reaction that involves an electrophilic substitution mechanism. The electronic factors in the isomerization process would therefore remain effectively unchanged while



Scheme 1.

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1,8-*peri*-interactions would be minimized. We report here on the synthesis and isomerization of the dioxolanes **5**–**7**.[7]

Our ideas[4,5] have been applied by Kaufman and coworkers both to the assembly of a model for the synthesis of the stephaoxocane alkaloids[8] and also to an investigation into the replacement of the two methyl substituents on our dioxolanes[4,5] with more complex groups.[9]

Results and Discussion

Syntheses of the Aryldioxolanes

2-Chloro-3-hydroxybenzaldehyde was obtained through regioselective chlorination of 3-hydroxybenzaldehyde by the method of Ginsberg.[10] Methylation afforded the methoxybenzaldehyde **8** in 87% yield and this was converted into a 3:1 mixture of the (*Z*)- and (*E*)-alkenes **9** and **10** in a combined yield of 97% on being allowed to react with ethyltriphenylphosphonium bromide in the presence of butyl lithium. In order to obtain stereochemically pure products in the subsequent reaction sequences a single stereochemistry was required for this alkene and the mixture was therefore treated with (bisacetonitrile)dichloropalladium(II), which transformed[11] the (*Z*)/(*E*) ratio into 1:24 in an 88% yield.

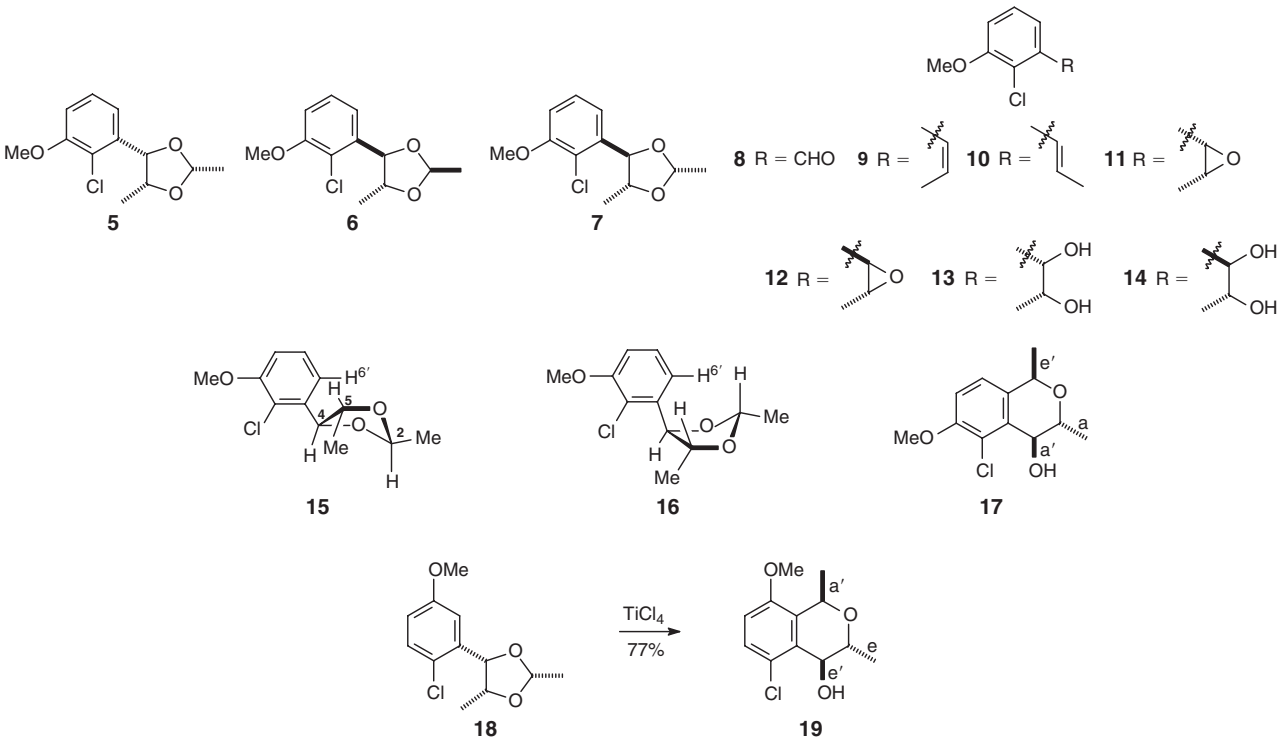
This mixture of alkenes highly enriched in the (*E*)-isomer was treated with *m*-chloroperoxybenzoic acid in the presence of solid sodium bicarbonate to furnish a 1:24 mixture of the *cis*- and *trans*-epoxides **11** and **12** in a yield of 86%. This epoxide mixture was ring-opened using dilute aqueous potassium hydroxide in dimethyl sulfoxide[12] to afford, after chromatography, the pure crystalline *erythro*-diol **13**, uncontaminated by the epimeric *threo*-diol, in an unoptimized yield of 27%. In the ^{1}H NMR spectrum the benzylic proton appeared at δ 5.26 as a doublet with a coupling constant of 3.2 Hz. Acetylation of this *erythro*-diol with 1,1-dimethoxyethane in the presence of a catalytic quantity of camphorsulfonic acid gave the all-*cis*-dioxolane **5** as the sole product in a yield of 94%. The structural assignment followed from its ^{1}H NMR spectrum that showed the three dioxolanyl ring protons as a doublet (J 7.2 Hz) at δ 5.48, a quartet (J 4.8 Hz) at δ 5.19, and a doublet of quartets (J 7.2 and J 6.3 Hz) at δ 4.55, corresponding to the protons 4-H, 2-H and 5-H respectively. The C-2 and C-5 methyl groups each appeared as a doublet, the former with a typical coupling constant of 4.8 Hz at δ 1.56 and the latter at δ 0.85 (J 6.3 Hz). The relative stereochemistry was adduced through comparison with other related all-*cis*-dioxolanes,[4,5] all of which were assembled as single diastereoisomers from their precursor *erythro*-diols.

For the C-2 epimeric compounds **6** and **7** the mixture of alkenes **9** and **10** highly enriched in the (*E*)-isomer was treated with a catalytic amount of osmium tetroxide in the presence of *N*-methylmorpholine *N*-oxide to afford the *threo*-diol **14** in 86% yield after chromatography that removed traces of the *erythro*-diol **13** arising from the small quantity of the (*Z*)-alkene **9** in the substrate. In the ^{1}H NMR spectrum the benzylic proton appeared at δ 5.00 as a doublet with a coupling constant of 5.3 Hz. A comparison of these spectral data with those for the *erythro*-stereoisomer **13** further confirmed the relative stereochemical assignments for the two diols since the chemical shifts for benzylic protons in *erythro*-isomers are known to resonate at lower field and have a smaller *vicinal* coupling constant than for the corresponding *threo*-compounds.[13]

Treatment of diol **14** with 1,1-dimethoxyethane and a catalytic quantity of camphorsulfonic acid afforded a 2:3 mixture of the C-2 epimeric dioxolanes **6** and **7** in 85% yield. This was separated into its two component epimers through careful preparative thin layer chromatography. Individual assignments were achieved through NOE difference spectroscopy that also supported the preferred conformations **15** and **16** for the minor and major products **6** and **7** respectively. Thus, for the former, irradiation of the C-5 methyl effected 4% and 7% enhancements for the protons 2-H and 4-H, while irradiation of the C-2 methyl led to 3% enhancement of the aromatic proton 6′-H. Enhancements of 3% and 6% for the proton 2-H and the C-5 methyl were observed on irradiation of 4-H. Irradiation of 2-H led to a 3% enhancement for both the proton 4-H and the C-5 methyl. Similar proximities supported the conformation **16** for the major isomer **7**, including a 5% enhancement of the aromatic proton 6′-H on irradiation of the proton 2-H.

Isomerization of the Aryldioxolanes

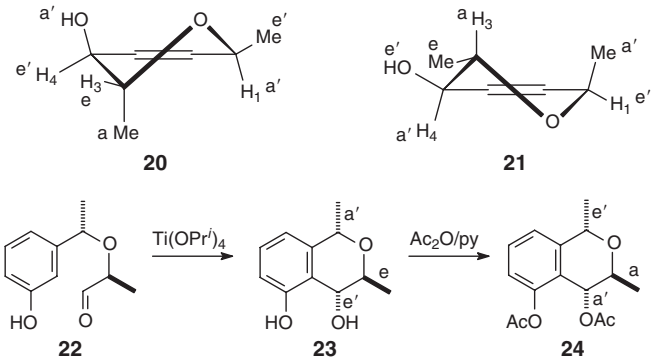
Treatment of the all-*cis*-dioxolane **5** in methylene dichloride with two equivalents of titanium(IV) chloride at −78°C afforded a single, virtually pure, 2-benzopyran in 76% yield. The ^{1}H NMR spectrum showed three one-proton signals for the three heterocyclic ring protons 1-H, 4-H, and 3-H as a quartet (J 6.4 Hz) at δ 4.85, a doublet (J 2.2 Hz) at δ 4.63, and a doublet of quartets (J 2.2 and 6.9 Hz) at δ 4.32 respectively. The small coupling constant of 2.2 Hz between the *vicinal* heterocyclic ring protons 3-H and 4-H deviated from those observed for all 2-benzopyrans arising through isomerization of all-*cis*-dioxolanes in our previous studies.[4,5] Since the stereochemistry at C-4 and C-5 in such dioxolanes is transferred unaltered to C-4 and C-3, respectively, in the product 2-benzopyrans, it followed that the substituents at these centres in the pyran **17** were *trans* as shown. This small coupling constant therefore indicated that the C-3 methyl and C-4 hydroxy groups were axial and pseudoaxial, as shown. On the other hand, the rearrangement of the isomeric all-*cis*-dioxolane **18**, which differs from the dioxolane **5** only in the aromatic substitution pattern, afforded the 2-benzopyran **19** in 77% yield[5] (Scheme 2). In this product, the ^{1}H NMR spectrum showed the much larger coupling constant of 6.0 Hz between the *vicinal* protons 3-H and 4-H, which showed that these protons were approximately *trans* diaxial, and, therefore, that the methyl and hydroxy groups at these centres were equatorial and pseudoequatorial, as shown. These experiments indicate that the dihydropyran rings of benzopyrans **17** and **19** adopt the two alternative half-chair conformations **20** and **21** respectively. This conclusion was supported by ^{1}H NMR NOE experiments. In an NOE difference spectrum obtained for compound **17**, irradiation of the C-3 methyl group led to a 9% enhancement of the proton



Scheme 2.

1-H, but no observable enhancement occurred for the proton 3-H upon irradiation of the C-1 methyl protons. For compound **19** a similar experiment showed the proximity between the C-1 methyl and 3-H,[5] but not between the C-3 methyl and 1-H.

This conformational difference between benzopyrans **17** and **19** can be accounted for in terms of differences in *peri*-interactions within these structural isomers. For compound **19** there are significant 4,5-*peri*-interactions between the hydroxy group and the chlorine substituent, as well as 1,8-*peri*-interactions between the methyl and methoxy groups. The pseudoaxial orientation of the C-1 methyl minimizes the latter interaction. The equatorial orientation of the C-3 methyl is typical of such molecules.[4,5] In isomer **17**, effective removal of the 1,8-*peri*-interactions in compound **19** through relocation of the C-8 methoxy while retaining the 4,5-*peri*-interactions induces the C-4 hydroxy group to minimize this remaining interaction by assuming the pseudoaxial orientation at the expense of the C-3 methyl becoming axial, and the C-1 methyl becomes pseudoequatorial through lack of a significant steric interaction with the proton 8-H. Recently we reported[7,14] on the only other example, to our knowledge, of a 2-benzopyran in which the C-3 methyl is axial. In that instance acetylation of the 2-benzopyran-4,5-diol **23**, obtained through the entirely diastereoselective cyclization of the asymmetric tethered lactaldehyde **22**, afforded the diacetate **24**. This acetylation was accompanied by the conformational inversion of the dihydropyran ring owing to increased 4,5-*peri*-interactions in the product diacetate **24** relative to the diol **23** (Scheme 3), in which mutual hydrogen bonding may also favour the pseudoequatorial orientation of



Scheme 3.

the C-4 hydroxyl group. The same observation was made for the related monoacetylation of the 5-*O*-methyl ether of **23**.[14]

Table 1 shows the effect of reaction time on the isomerization of the all-*cis*-dioxolane **5** into the 2-benzopyran **17**.

Similar isomerization of the 2:3 mixture of C-2 epimeric 4,5-*trans*-dioxolanes **6** and **7** afforded the all-*cis*-2-benzopyran **25** as the sole product over a temperature range of −78 to +25°C. The yields for these reactions at various temperatures were consistently high (∼90%). The stereochemistry of the product was assigned on the basis of the ^{1}H NMR spectrum that showed, in particular, both a small coupling constant (*J* 1.5 Hz) between the *vicinal* protons 3-H and 4-H and also a doublet of quartets resonating at *δ* 3.77 for the heterocyclic proton 3-H. This latter relatively shielded value is typical for the 3-H proton in *cis*-1,3-dimethyl-2-benzopyrans compared to their *trans*-1,3 epimers.[4,5,15,16] The related values for the pair of C-1 epimeric 2-benzopyrans

Table 1. Effect of reaction duration on isomerization of the dioxolane 5

Entry	Conditions[A] 2 equiv. $TiCl_4$	Dioxolane product **5**[C] [%]	2-Benzopyran product **17**[C] [%]
1	−78°C,[B] 10 min	75	25
2	−78°C,[B] 20 min	12	88
3	−78°C,[B] 30 min	1	99

[A] Stereochemically pure *cis*-4,5-disubstituted phenyldioxolane **5** in dry methylene dichloride, at a concentration of 6×10^{-3} mol L^{-1}.
[B] Temperature at which the reaction was quenched with methanol.
[C] Ratios and product percentages quoted were determined by ^1H NMR spectroscopic analysis.

Table 2. Effect of reaction conditions on isomerization of the isomeric mixture of dioxolanes 6 and 7

Entry	Conditions[A] 2 equiv. $TiCl_4$	Dioxolane products **6** and **7**[C] [%]	2-Benzopyran product **25**[C] [%]
1	−78°C,[B] 20 min	2	98
2	−78°C,[B] 30 min	2	98
3	−78°C,[B] 30 min	1	99
4	−78°C,[B] 60 min	2	98
5	−30°C,[B] 30 min	5	95
6	0°C,[B] 30 min	3	97
7	25°C,[B] 30 min	2	98

[A] 2:3 Diastereomeric mixture of dioxolanes **6** and **7** in dry methylene dichloride, at a concentration of 3×10^{-3} mol L^{-1}.
[B] Temperature at which the reaction was quenched with methanol.
[C] Dioxolanes and product percentages quoted were determined by ^1H NMR spectroscopic analysis.

2 and **3**, which differ from **25** only in the aromatic regiochemistry, are δ 3.68 and δ 4.11 respectively.[5] Table 2 shows the results of these isomerizations at various temperatures. None of the C-1 epimer was observed throughout this temperature range. There is therefore a major stereochemical difference in the isomerization[5] of the pair of C-2 epimeric dioxolanes **1** and **4**, where the C-1 orientation changed dramatically over the small temperature range −95–78°C in comparison with the corresponding pair of regioisomeric dioxolanes **6** and **7**, where the C-1 stereochemistry remained constant over a temperature range of some 100°C. Each of these experiments was conducted separately, rather than removing aliquots at different temperatures and times, in order to ensure that each reaction was quenched at the temperature quoted.

We suggest that differences arise because the significant 1,8-*peri*-interactions present in benzopyran **2** are largely absent in the regioisomer **25**. This interpretation needs to be treated with caution, however, since we have previously shown that the all-*cis*-*meta*-dimethoxyphenyldioxolane **26** (Scheme 4) isomerizes to a 4:1 mixture of the 2-benzopyrans **27** and **28** at −78°C, whereas at −30°C this ratio was reversed completely to 1:7,[4] where the C-1 methyl was pseudoequatorial in the major isomer **28** at the higher temperature. Furthermore, the ratio of benzopyrans recovered after treatment of a 4:1 mixture of **27** and **28** with titanium(IV) chloride at higher temperatures contained less of the component **27**. This latter fact indicates that the benzopyrans **27** and **28** are thermodynamic products, whereas compounds **2** and **3** are known to be kinetic products,[5] a difference that may arise through the combined influence of the two aryl methoxy substituents facilitating the ring-opening of the titanium-coordinated benzopyran **29** to afford the quinomethane system **30**. Ring-closure of **30** would lead to either C-1 stereoisomer of **29**, and thence to an altered ratio of **27** to **28** (Scheme 5).

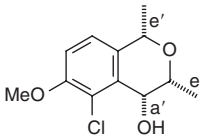
Careful chromatography afforded each of the individual C-2 epimers **6** and **7**. The results of isomerization of the minor diastereoisomer **6** with titanium(IV) chloride at −78°C are shown in Table 3. Once again, compound **25** was the only 2-benzopyran formed. For shorter times, significant quantities of starting dioxolane were isolated as a mixture of the C-2 epimers **6** and **7** at this temperature, with the proportion of the alternative isomer **7** increasing over longer reaction times. The reason for this epimerization has been postulated previously for the individual regioisomeric dioxolanes **1** and **4**.[5]

The results for the related isomerization of the pure dioxolane **7** are shown in Table 4. Once again, the sole 2-benzopyran produced was compound **25**. A comparison of Tables 3 and 4 shows that the isomerization of the major C-2 epimer **7** occurs much faster than that for the minor epimer **6**, and the reason for this has been given previously for the dioxolanes **1** and **4**.[5]

Conclusions

The 4-(2′-chloro-3′-methoxyphenyl)-2,5-dimethyl-1,3-dioxolanes **5–7** were isomerized in high yield to 2-benzopyrans, using two equivalents of titanium(IV) chloride. The all-*cis*-dioxolane **5** afforded the product **17**, in which the preferred conformation of the dihydropyran ring involves the C-3 methyl group being axial as a consequence of weak 1,8- and significant 4,5-*peri*-interactions favouring a pseudoequatorial orientation for the C-1 methyl and a pseudoaxial orientation for the C-4 hydroxy group. Isomerization of the 2:3 mixture of C-2 epimeric 4,5-*trans*-dioxolanes **6** and **7** afforded the all-*cis*- 2-benzopyran **25** as the sole product, as did each of the individual components **6** and **7** of the mixture. In contrast to the observations for the isomerization of the dioxolanes **1** and **4**, which each gave the C-1 pseudoequatorial benzopyran **2** at −95°C and its C-1 pseudoaxial epimer **3** at −78°C, the pseudoequatorial stereochemistry at C-1 in the product **25** arising from the isomerization of **6** and **7** remained unchanged over the temperature range of −78 to +25°C. It is assumed, therefore, that the change in the former cases arises from the significant 1,8-*peri*-interactions in the benzopyran **2** that are reduced in its epimer **3**. These interactions are insignificant in regioisomer **25**.

It was noted previously[5] that in those isomerizations in which a single stereoisomer of the 2-benzopyran was formed, the substituents at C-1 and C-4 are *cis*-related i.e. one is pseudoaxial while the other is pseudoequatorial. The stereochemistry of each of the benzopyran products **17** and **25** in this study conforms to this observation.



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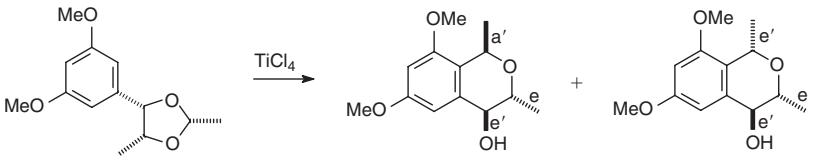
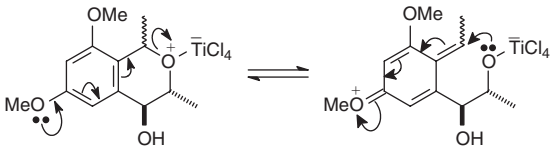


26 **27** **28**

Scheme 4.



29 **30**

Scheme 5.

Experimental

General

Melting points were determined on a Reichert hot stage apparatus and are uncorrected. Infrared spectra were recorded as KBr disks and nujol mulls for solids and as thin films between NaCl plates for oils, using a Perkin Elmer 1720-X Fourier transform spectrometer or a Nicolet Fourier transform spectrometer. Nuclear magnetic resonance (NMR) spectra were recorded using a Bruker Advance DPX-300 spectrometer (^{1}H, 300 MHz; ^{13}C, 75.5 MHz). The spectra were routinely run at ambient temperature in deuterated chloroform ($CDCl_3$) solution, with the internal standard tetramethylsilane (TMS) at δ 0.00 ppm for both the ^{1}H and ^{13}C NMR spectra. The signals in the ^{13}C NMR spectra were assigned with the help of the DEPT technique and assignments with the same superscripts are interchangeable. Mass spectra were obtained on a Hewlett Packard 5986 spectrometer operating in the electron impact mode at 35 eV. High resolution mass spectra were obtained on a V. G. Autospec high resolution mass spectrometer. Elemental analyses were performed by Canadian Microanalytical Service Co. Standard work-up refers to extraction with an organic solvent, drying the organic layer using anhydrous magnesium sulfate ($MgSO_4$) and concentration under reduced pressure. Column chromatography refers to columns dry packed with Merck silica gel 60 (70–230 mesh) as the stationary phase. Preadsorption was carried out on Merck silica gel 60 (35–70 mesh). Preparative thin layer chromatography (PLC) was performed using Camag silica gel as a 0.3 mm thick layer on glass plates (20 × 20 cm). All solvents were purified by distillation and, if required, were dried using standard methods.

2-Chloro-3-hydroxybenzaldehyde

tert-Butyl hypochlorite (40.59 g, 0.37 mol) was added dropwise to *meta*-hydroxybenzaldehyde (43.690 g, 0.36 mol) dissolved in 90% aqueous acetic acid (100 mL). After stirring for 2 h, the resultant precipitate was filtered and recrystallized from 50% aqueous acetic acid to afford the product (30.842 g, 55%) as light tan crystals, mp 137–138°C (lit.[10] 139°C). ν_{max} (KBr disk)/cm^{-1} 3151 (O–H), 1669 (C=O), 1567 (C=C). δ_H 5.87 (1H, s, OH), 7.29 (1H, dd *J* 2.1 & 8.1, 4-H), 7.34 (1H, dd, *J* 7.3 & 8.1, 5-H), 7.53 (1H, dd, *J* 2.1 & 7.3, 6-H), 10.39 (1H, s, CHO). δ_C 121.8 (C-5)[a], 122.1 (C-6)[a], 125.9 (C-1), 128.1 (C-4)[a], 132.7 (C-2), 152.1 (C-3), 189.3 (CHO).

Table 3. Effect of reaction duration on isomerization of the dioxolane 6

Entry	Conditions[A] 2 equiv. $TiCl_4$	Ratio of dioxolane products **6**:**7**[C]	Dioxolane products **6** and **7**[C] [%]	2-Benzopyran product **25**[C] [%]
1	−78°C,[B] 10 min	6:1	75	25
2	−78°C,[B] 20 min	5:1	30	70
3	−78°C,[B] 30 min	–	3	97
4	−78°C,[B] 60 min	3:1	9	91

[A] Stereochemically pure *trans*-4,5-disubstituted phenyldioxolane **6** in dry methylene dichloride at a concentration of 6×10^{-3} mol L^{-1}.
[B] Temperature at which the reaction was quenched with methanol.
[C] Ratios and product percentages quoted were determined by ^{1}H NMR spectroscopic analysis.

Table 4. Effect of reaction duration on isomerization of the dioxolane 7

Entry	Conditions[A] 2 equiv. $TiCl_4$	Dioxolane product **7**[C] [%]	2-Benzopyran product **25**[C] [%]
1	−78°C,[B] 2 min	2	98
2	−78°C,[B] 3 min	2	98
3	−78°C,[B] 10 min	0	100
4	−78°C,[B] 30 min	2	98

[A] Stereochemically pure *trans*-4,5-disubstituted phenyldioxolane **7** in dry methylene dichloride at a concentration of 6×10^{-3} mol L^{-1}.
[B] Temperature at which the reaction was quenched with methanol.
[C] Ratios and product percentages quoted were determined by ^{1}H NMR spectroscopic analysis.

*2-Chloro-3-methoxybenzaldehyde **8***

Dimethyl sulfate (3.25 mL, 19.47 mmol) was added to a solution of 2-chloro-3-hydroxybenzaldehyde (1.016 g, 6.49 mmol) and anhydrous potassium carbonate (2.748 g, 19.88 mmol) in dry dimethylformamide (80 mL). The mixture was stirred at 60°C in an atmosphere of argon for 5 h. The resultant mixture was cooled to room temperature, diluted with water, and filtered. The filtrate was further diluted with water and extracted with diethyl ether. The ether extract was washed with ammonia solution (25%) and then twice with water. The residue obtained upon standard work-up was chromatographed (20% ethyl acetate–hexane) to give the aldehyde **8** (968 mg, 87%) as white needles, mp 56–57°C (Found: C 56.05, H 4.1, M$^+$ 170.0129. $C_8H_7ClO_2$ requires C 56.35, H 4.15, M 170.0135). ν_{max} (KBr disk)/cm^{-1} 1686 (C=O), 1572 & 1526 (C=C). δ_H 3.96 (3H, s, OCH_3), 7.17 (1H, dd, *J* 1.5 & 8.2, 4-H), 7.36 (1H, dd, *J* 7.8 & 8.2, 5-H), 7.53 (1H, dd, *J* 1.5 & 7.8, 6-H), 10.53 (1H, s, CHO). δ_C 56.6 (OCH_3), 117.0 (C-5)[a], 120.7 (C-6)[a], 125.9 (C-1), 127.5 (C-4)[a], 133.6 (C-2), 155.5 (C-3), 190.2 (CHO). *m/z* 172

[M^+ (^{37}Cl), 32%], 170 [M^+ (^{35}Cl), 41], 171 (91), 169 (100), 126 (18), 99 (28), 97 (19), 77 (26), 71 (32), 69 (34), 57 (55).

(Z)- and (E)-1-(2′-Chloro-3′-methoxyphenyl)prop-1-enes ***9*** *and* ***10***

Sodium hydride (60% dispersion in mineral oil, 1.658 g) was stirred with dry dimethyl sulfoxide (4 mL) and dry tetrahydrofuran (16 mL) at 60°C for 2 h in an atmosphere of nitrogen. The mixture was cooled to room temperature and ethyltriphenylphosphonium bromide (12.858 g, 34.72 mmol) in dry tetrahydrofuran (40 mL) was added to the mixture and stirred at room temperature for 15 min. The aldehyde **8** (4.000 g, 23.45 mmol) in dry tetrahydrofuran was added dropwise to the mixture and stirred for a further 1 h at 60°C. The cooled reaction mixture was filtered and washed with dry tetrahydrofuran. The residue obtained upon standard work-up was chromatographed (20% ethyl acetate–hexane) to give a 3:1 mixture of (*Z*)- and (*E*)-olefins **9** and **10** (4.174 g, 97%) as yellow oil. This mixture in dry methylene dichloride (140 mL) was treated with bis(acetonitrile)dichloropalladium(II) (205 mg), and boiled for 7 days. The reaction mixture was filtered, then evaporated to afford a residue that was chromatographed (20% ethyl acetate–hexane) to give the (*E*)-olefin **10** (96% by ^{1}H NMR) contaminated with the (*Z*)-olefin (**9**) (4% by ^{1}H NMR) (Found: M^+ 182.0503. $C_{10}H_{11}ClO$ requires M 182.0498). ν_{max} (thin film)/cm^{-1} 1569 & 1468 (C=C). δ_H (for **10**) 1.92 (3H, dd, *J* 1.7 & 6.6, CH_3), 3.89 (3H, s, OCH_3), 6.22 (1H, dq, *J* 6.6 & 15.7, 2-H), 6.79 (1H, dd, *J* 2.0 & 7.4, 6′-H), 6.82 (1H, dq, *J* 1.7 & 15.7, 1-H), 7.11 (1H, dd, *J* 2.0 & 7.9, 4′-H), 7.15 (1H, dd, *J* 7.4 & 7.9, 5′-H). δ_C (for **10**) 18.8 (CH_3), 56.2 (OCH_3), 109.9 (C-5′)[a], 118.6 (C-6′)[a], 126.8 (C-2)[b], 127.4 (C-4′)[a], 128.4 (C-1)[b], 129.1 (C-1′), 137.5 (C-2′), 155.2 (C-3′). *m/z* 184 [M^+ (^{37}Cl), 24%], 182 [M^+ (^{35}Cl), 74], 147 (68), 132 (15), 115 (29), 103 (34), 97 (34), 91 (56), 86 (54), 85 (48), 83 (33), 81 (46), 77 (33), 71 (45), 70 (32), 69 (44), 57 (100), 56 (31). Inspection of the 3:1 mixture indicated the following data for the (*Z*)-olefin **9**: δ_H 1.78 (3H, dd, *J* 1.8 & 7.0, CH_3), 3.90 (3H, s, OCH_3), 5.90 (1H, dq, *J* 7.0 & 11.5, 2-H), 6.53 (3H, dq, *J* 1.8 & 11.5, 1-H), 6.93 (1H, dd, *J* 2.0 & 7.6, 6′-H), 7.10 (1H, dd, *J* 2.0 & 8.0, 4′-H), 7.18 (1H, dd, *J* 7.6 & 8.0, 5′-H).

cis- *and* trans-*1-(2′-Chloro-3′-methoxyphenyl)-1,2-epoxypropanes* ***11*** *and* ***12***

meta-Chloroperoxybenzoic acid (1.204 mg, 6.98 mmol) in chloroform (45 mL) at 0°C was added dropwise to the 1:24 mixture of olefins **9** and **10** (908 mg, 4.97 mmol) in chloroform (20 mL), and the solution was stirred with anhydrous sodium hydrogencarbonate (219 mg) at room temperature for 44 h. The reaction mixture was filtered and the filtrate was poured into saturated aqueous sodium hydrogencarbonate solution. The organic layer was separated and the aqueous layer was extracted with cold chloroform. A 1:24 mixture of epoxides **11** and **12** (844 mg, 86%) was obtained upon standard work-up as an orange oil (Found: C 60.35, H 5.7, [FAB MS]: $(M+1)^+$ 199.0546. $C_{10}H_{11}ClO_2$ requires C 60.45, H 5.6, (M + 1) 199.0526). ν_{max} (thin film)/cm^{-1} 1576 & 1474 (C=C). δ_H (for **12**) 1.49 (3H, d, *J* 5.2, CH_3), 2.88 (1H, dq, *J* 2.0 & 5.2, 2-H), 3.90 (3H, s, OCH_3), 3.93 (1H, d, *J* 2.0, 1-H), 6.86 (2H, dd, *J* 1.5 & 8.0, 4′-H & 6′-H), 7.20 (1H, t, *J* 8.0, 5′-H). δ_C (for **12**) 17.8 (CH_3), 56.2 (OCH_3), 57.1 (C-2)[a], 58.4 (C-1)[a], 111.1 (C-5′)[b], 117.5 (C-6′)[b], 121.3 (C-1′), 127.4 (C-4′)[b], 137.4 (C-2′), 154.8 (C-3′). *m/z* 201 [$(M+1)^+$ (^{37}Cl), 19%], 200 (23), 199 [$(M+1)^+$ (^{35}Cl), 54], 198 (54), 156 (14), 155 (41), 154 (100), 151 (10), 149 (40), 139 (35), 138 (53), 137 (99), 136 (85), 109 (13), 107 (36), 91 (34), 81 (33), 77 (25), 71 (25), 69 (54), 67 (31), 57 (77), 55 (64), 43 (65), 41 (73).

rel-*(1S,2R)-1-(2′-Chloro-3′-methoxyphenyl)propane-1,2-diol* ***13***

The 1:24 mixture of epoxides **11** and **12** (360 mg, 1.81 mmol) in dry dimethyl sulphoxide (15 mL) and aqueous potassium hydroxide solution (0.4 M, 6.1 mL) was stirred at 80°C. After 24 h, the reaction mixture was cooled to room temperature and poured into water. The organic layer was separated and the aqueous layer was extracted with ethyl acetate. The residue obtained upon standard work-up was chromatographed (50% ethyl acetate–hexane) to give the diol **13** (107 mg, 27%) as white crystals, mp 93–95°C (Found C 54.9, H 5.85, [FAB MS]: $(M+1-H_2O)^+$ 199.0533. $C_{10}H_{13}ClO_3$ requires C 55.45, H 6.05, $(M+1-H_2O)$ 199.0526). ν_{max} (KBr disk)/cm^{-1} 2924 (O–H), 1462 (C=C). δ_H 1.06 (3H, d, *J* 6.4, CH_3), 1.98 (1H, d, *J* 5.3, 2-OH), 2.53 (1H, d, *J* 3.2, 1-OH), 3.91 (3H, s, OCH_3), 4.23 (1H, m, 2-H), 5.26 (1H, t, *J* 3.2, 1-H), 6.89 (1H, dd, *J* 1.9 & 7.8, 6′-H), 7.22 (1H, dd, *J* 1.9 & 7.8, 4′-H), 7.26 (1H, t, *J* 7.8, 5′-H). δ_C 15.2 (CH_3), 55.0 (OCH_3), 68.0 (C-2), 72.5 (C-1), 109.7 (C-5′)[a], 118.6 (C-6′)[a], 124.7 (C-1′), 126.0 (C-4′)[a], 138.2 (C-2′), 153.6 (C-3′). *m/z* 201 [$(M+1-H_2O)^+$ (^{37}Cl), 33%], 199 [$(M+1-H_2O)^+$ (^{35}Cl), 100], 174 (12), 172 (39).

rel-*(2R,4S,5R)-4-(2′-Chloro-3′-methoxyphenyl)-2,5-dimethyl-1,3-dioxolane* ***5***

1,1-Dimethoxyethane (60 μL, 0.57 mmol) and (±)-10-camphorsulfonic acid (6 mg, 0.03 mmol) were added to diol **13** in methylene dichloride (12 mL). The solution was boiled for 3 h and quenched with saturated aqueous sodium hydrogencarbonate solution. The organic layer was separated and the aqueous layer was extracted with more methylene dichloride. The residue obtained upon standard work-up was chromatographed (10% ethyl acetate–hexane) to afford the dioxolane **5** (78 mg, 94%) as a colourless oil (Found C 58.95, H 6.3, M^+ 242.0721. $C_{12}H_{15}ClO_3$ requires C 59.4, H 6.25, M 242.0710). ν_{max} (thin film)/cm^{-1} 1585 & 1467 (C=C). δ_H 0.85 (3H, d, *J* 6.3, 5-CH_3), 1.56 (3H, d, *J* 4.8, 2-CH_3), 3.90 (3H, s, OCH_3), 4.55 (1H, dq, *J* 6.3 & 7.2, 5-H), 5.19 (1H, q, *J* 4.8, 2-H), 5.48 (1H, d, *J* 7.2, 4-H), 6.88 (1H, dd, *J* 1.5 & 7.9, 6′-H), 7.17 (1H, dd, *J* 1.5 & 7.9, 4′-H), 7.25 (1H, t, *J* 7.9, 5′-H). δ_C 16.4 (5-CH_3), 19.7 (2-CH_3), 56.2 (OCH_3), 75.2 (C-5), 77.7 (C-4), 100.5 (C-2), 110.9 (C-5′)[a], 119.3 (C-6′)[a], 120.1 (C-1′), 127.1 (C-4′)[a], 137.9 (C-2′), 154.8 (C-3′). *m/z* 244 [M^+ (^{37}Cl), 5%], 242 [M^+ (^{35}Cl), 14], 200 (34), 198 (100), 269 (35), 167 (35), 163 (31), 91 (40), 86 (33), 84 (48), 83 (33), 81 (26), 77 (15), 72 (34), 69 (37), 57 (33).

rel-*(1R,2R)-1-(2′-Chloro-3′-methoxyphenyl)propane-1,2-diol* ***14***

N-Methylmorpholine *N*-oxide (166 mg, 1.42 mmol) and osmium tetroxide (5 mg) in *tert*-butyl alcohol (1 mL) were added to the 1:24 mixture of olefins **9** and **10** (204 g, 1.12 mmol) in a 2:1 mixture of acetone–water (6 mL). The mixture was stirred in an atmosphere of nitrogen for 24 h. After this, acetone was removed under vacuum at room temperature. The aqueous layer was added to dilute hydrochloric acid (2 M) and extracted into ethyl acetate. The residue obtained upon standard work-up was chromatographed (50% ethyl acetate–hexane) to give the diol **14** (207 mg, 86%) as white crystals, mp 109–110°C (Found C 55.8, H 6.15, M^+ 216.0555. $C_{10}H_{13}ClO_3$ requires C 55.45, H 6.05, M 216.0553). ν_{max} (KBr disk)/cm^{-1} 3385 (O–H), 1584, 1524, & 1466 (C=C). δ_H 1.20 (3H, d, *J* 6.4, CH_3), 2.28 (1H, d, *J* 4.0, 2-OH), 2.72 (1H, d, *J* 5.3, 1-OH), 3.91 (3H, s, OCH_3), 3.97 (1H, m, 2-H), 5.00 (1H, t, *J* 5.3, 1-H), 6.89 (1H, dd, *J* 1.4 & 8.0, 6′-H), 7.12 (1H, dd, *J* 1.4 & 8.0, 4′-H), 7.27 (1H, t, *J* 8.0, 5′-H). δ_C 18.9 (CH_3), 56.3 (OCH_3), 71.3 (C-2), 74.5 (C-1), 111.2 (C-5′)[a], 119.6 (C-6′)[a], 121.0 (C-1′), 127.4 (C-4′)[a], 140.5 (C-2′), 155.0 (C-3′). *m/z* 218 [M^+ (^{37}Cl), 3%], 216 [M^+ (^{35}Cl), 7], 174 (31), 172 (100), 145 (13), 143 (41), 137 (35), 109 (21), 108 (32), 77 (21).

rel-*(2S,4R,5R)- and* rel-*(2R,4R,5R)-4-(2′-Chloro-3′-methoxyphenyl)-2,5-dimethyl-1,3-dioxolanes* ***6*** *and* ***7***

The diol **14** (2.000 g, 9.23 mmol) in dry methylene dichloride (200 mL) was treated with 1,1-dimethoxyethane (1.0 mL, 9.43 mmol) and (±)-10-camphorsulfonic acid (151 mg, 0.65 mmol) and the solution was boiled for 24 h in an atmosphere of nitrogen. The reaction mixture was quenched with saturated aqueous sodium hydrogencarbonate solution. The organic layer was separated and the aqueous layer was extracted into more methylene dichloride. The residue obtained upon standard work-up was chromatographed (10% ethyl acetate–hexane) to afford the 2:3 mixture of dioxolanes **6** and **7** (1.910 g, 85%) as pale yellow crystals. The mixture was separated by preparative layer chromatography that afforded the dioxolane **6**, the minor product with the slightly higher R_F, as a yellow oil (Found C 59.4, H 6.3, [FAB MS]: $(M-1)^+$ 241.0647. $C_{12}H_{15}ClO_3$ requires C 59.4, H 6.25, (M − 1) 241.0631). ν_{max} (thin film)/cm^{-1} 1577 & 1472 (C=C). δ_H 1.43 (3H, d, *J* 6.3, 5-CH_3), 1.53 (3H, d, *J* 4.8, 2-CH_3), 3.91 (3H, s, OCH_3), 4.03 (1H, dq, *J* 6.0 & 6.3, 5-H), 5.11 (1H, d, *J* 6.0, 4-H), 5.42 (1H, q, *J* 4.8, 2-H), 6.87 (1H, dd,

J 1.9 & 7.6, 6′-H), 7.22 (1H, dd, *J* 1.9 & 7.9, 4′-H), 7.26 (1H, dd, *J* 7.6 & 7.9, 5′-H). δ_C 17.0 (5-CH_3), 19.1 (2-CH_3), 55.1 (OCH_3), 78.7 (C-5), 80.2 (C-4), 99.6 (C-2), 110.0 (C-5′)[a], 118.1 (C-6′)[a], 125.9 (C-1′), 126.3 (C-4′)[a], 137.8 (C-2′), 153.8 (C-3′). *m/z* 243 [$(M-1)^+$ (^{37}Cl), 24%], 241 [$(M-1)^+$ (^{35}Cl), 36%], 201 (31), 200 (40), 199 (100), 198 (82), 149 (24), 97 (17), 83 (33), 67 (17), 57 (79), 55 (31), 43 (64), 41 (50), 29 (31), 27 (27). The major epimer **7** at a slightly lower R_F was obtained as white crystals, mp 78–79°C (hexane) (Found: C 59.95, H 6.25, [FAB MS]: $(M+1)^+$ 243.0770. $C_{12}H_{15}ClO_3$ requires C 59.4, H 6.25, (M + 1) 243.0788). ν_{max} (thin film)/cm^{-1} 1462 (C=C). δ_H 1.47 (3H, d, *J* 6.1, 5-CH_3), 1.49 (3H, d, *J* 4.7, 2-CH_3), 3.91 (3H, s, OCH_3), 3.93 (1H, dq, *J* 6.1 & 7.4, 5-H), 5.08 (1H, d, *J* 7.4, 4-H), 5.48 (1H, q, *J* 4.7, 2-H), 6.88 (1H, dd, *J* 1.4 & 8.0, 4′-H), 7.14 (1H, dd, *J* 1.4 & 8.0, 6′-H), 7.26 (1H, t, *J* 8.0, 5′-H). δ_C 19.4 (5-CH_3), 22.5 (2-CH_3), 58.0 (OCH_3), 82.2 (C-5), 83.2 (C-4), 104.0 (C-2), 112.8 (C-5′)[a], 121.0 (C-6′)[a], 127.6 (C-1′), 129.2 (C-4′)[a], 140.7 (C-2′), 156.8 (C-3′). *m/z* 243 [$(M+1)^+$ (^{37}Cl), 12%], 241 [$(M+1)^+$ (^{35}Cl), 17], 201 (17), 200 (18), 199 (54), 198 (38), 149 (44), 95 (32), 83 (39), 81 (39), 71 (40), 69 (79), 57 (95), 55 (100), 43 (97), 41 (75), 29 (46).

rel-*(1*R*,3*R*,4*S*)-5-Chloro-4-hydroxy-6-methoxy-1,3-dimethyl-2-benzopyran* ***17***

Titanium(IV) chloride (48 μL, 0.44 mmol) was added to a stirred solution of dioxolane **5** (50 mg, 0.21 mmol) in dry methylene dichloride (33.5 mL) at −78°C in an atmosphere of nitrogen. After 30 min the reaction was quenched at this temperature with dry methanol (0.1 mL). The quenched solution was neutralized with saturated aqueous sodium hydrogencarbonate solution, washed with water, dried, and evaporated to afford the 2-benzopyran **17** (38 mg, 76%) as a pale yellow oil (Found: M^+ 242.0715. $C_{12}H_{15}ClO_3$ requires M 242.0710). δ_H 1.21 (3H, d, *J* 6.9, 3-CH_3), 1.53 (3H, d, *J* 6.4, 1-CH_3), 3.91 (3H, s, OCH_3), 4.32 (1H, dq, *J* 2.2 & 6.9, 3-H), 4.63 (1H, d, *J* 2.2, 4-H), 4.85 (1H, q, *J* 6.4, 1-H), 6.92 (1H, d, *J* 8.6, 7-H), 7.01 (1H, d, *J* 8.6, 8-H). δ_C 15.3 (3-CH_3), 22.0 (1-CH_3), 56.1 (OCH_3), 65.6 (C-4)[a], 66.8 (C-1)[a], 72.4 (C-3)[a], 111.8 (C-7), 119.6 (C-8a), 123.0 (C-8), 123.5 (C-4a), 132.4 (C-5), 153.7 (C-6). *m/z* 244 [M^+ (^{37}Cl), 4%], 242 [M^+ (^{35}Cl), 13], 243 (15), 241 (42), 227 (26), 225 (60), 223 (31), 213 (34), 211 (32), 200 (24), 199 (42), 198 (99), 197 (75), 196 (100), 195 (62), 171 (21), 169 (44), 89 (18).

rel-*(1*S*,3*R*,4*R*)-5-Chloro-4-hydroxy-6-methoxy-1,3-dimethyl-2-benzopyran* ***25***

Titanium(IV) chloride (94 μL, 0.86 mmol) was added to a stirred solution of the 2:3 mixture of dioxolanes **6** and **7** (106 mg, 0.44 mmol) in dry methylene dichloride (120 mL) at −78°C in an atmosphere of nitrogen. After 30 min the reaction was quenched at this temperature with dry methanol (0.1 mL). The resultant solution was neutralized with saturated aqueous sodium hydrogencarbonate solution, washed with water, dried, and evaporated to afford the 2-benzopyran **25** (96 mg, 91%) as a colourless oil (Found [FAB MS]: $(M-1)^+$ 241.0655. $C_{12}H_{15}ClO_3$ requires (M − 1) 241.0631). δ_H 1.44 (3H, d, *J* 6.4, 3-CH_3), 1.55 (3H, d, *J* 6.4, 1-CH_3), 3.77 (1H, dq, *J* 1.5 & 6.4, 3-H), 3.91 (3H, s, OCH_3), 4.62 (1H, d, *J* 1.5, 4-H), 4.77 (1H, q, *J* 6.4, 1-H), 6.92 (1H, d, *J* 8.6, 7-H), 7.04 (1H, d, *J* 8.6, 8-H). δ_C 16.9 (3-CH_3), 21.9 (1-CH_3), 56.4 (OCH_3), 65.9 (C-4)[a], 73.0 (C-1)[a], 73.8 (C-3)[a], 112.1 (C-7), 122.9 (C-8a), 123.6 (C-8), 133.1 (C-4a), 135.3 (C-5), 153.9 (C-6). *m/z* 243 [$(M-1)^+$ (^{37}Cl), 38%], 241 [$(M-1)^+$ (^{35}Cl), 100], 227 (11), 225 (36), 149 (61), 81 (27), 69 (57), 57 (68), 43 (61), 41 (52).

Isomerization of Dioxolane ***6***

The dioxolane **6** (40 mg, 0.16 mmol) in dry methylene dichloride (27 mL) was stirred with titanium(IV) chloride (38 μL, 0.35 mmol) at −78°C in an atmosphere of nitrogen. The reaction mixture was quenched at this temperature with dry methanol (0.1 mL) after the time duration shown in Table 3. The quenched reaction solutions were neutralized with saturated aqueous sodium hydrogencarbonate solution, washed with water, dried, and evaporated. The residues were analyzed by ^{1}H NMR spectroscopy with the results given in Table 3.

Isomerization of Dioxolane 7

To the stirred solutions of dioxolane **7** (41 mg, 0.16 mmol) in dry methylene dichloride (26.5 mL), titanium(IV) chloride (32 μL, 0.29 mmol) was added at −78°C in an atmosphere of nitrogen. The reaction mixture was quenched at this temperature with dry methanol (0.1 mL) after the time duration detailed in Table 4. The quenched reaction solutions were neutralized with saturated aqueous sodium hydrogencarbonate solution, washed with water, dried, and evaporated. The residues were analyzed by ^{1}H NMR spectroscopy with the results given in Table 4.

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