

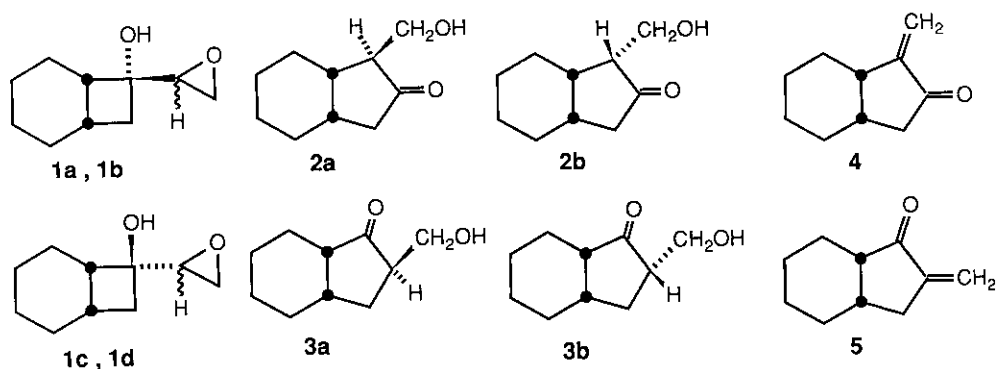
REGIO AND STERESELECTIVE REARRANGEMENTS OF STEREOISOMERIC
7-OXIRYLBICYCLO[4.2.0]OCTAN-7-OLS

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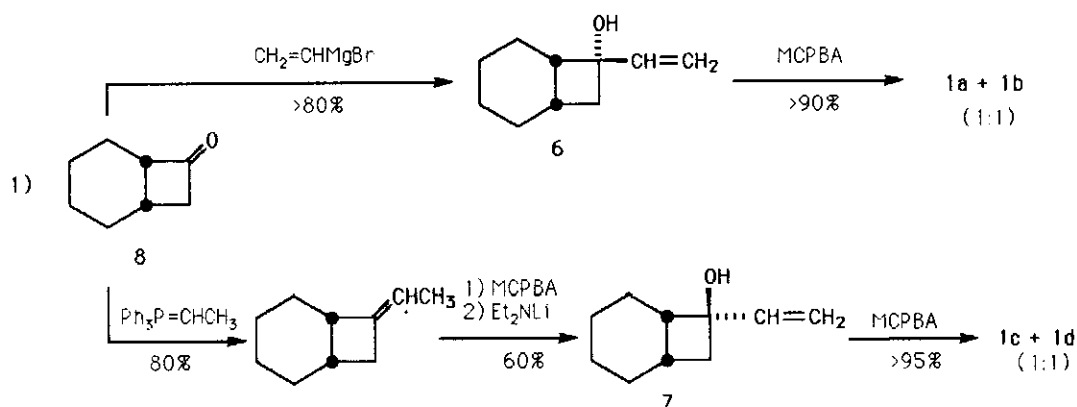
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Abstract—The four racemic diastereomers of the title compound (**1a** through **1d**) have been prepared by epoxidation of related vinyl cyclobutanols (**6** and **7**). Each epoxy alcohol is converted to a corresponding halohydrin (**9a** through **9d**) by magnesium bromide, and this transformation is reversed by the action of methanolic base. Mild treatment of the title compounds with boron trifluoride induced regio and stereoselective rearrangement to ring-expanded hydroxymethyl-substituted ketones (**2b**, **2a** and **3a** from **1a**, **1c** and **1d** respectively). Isomer **1b** did not react. Structural assignments were made on the strength of β -elimination of these ketols to enones **4** and **5**, as well as reduction to cis and trans diols **10** and **11**.

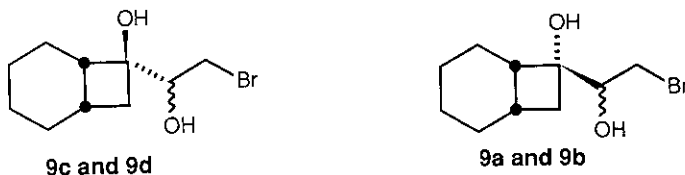
Anionotropic rearrangements involving carbocation-like species have been studied by organic chemists for over five decades¹. Our present understanding of the mechanism, selectivity and stereochemistry of such reactions² should permit the design of effective synthetic applications. In this context our interest in the use of strained ring compounds as intermediates in synthesis has led us to examine some acid-catalyzed reactions of the stereoisomeric epoxides (**1a** through **1d**) derived from 7-vinylbicyclo[4.2.0]octan-7-ol. The expected products from these reactions were the α -hydroxymethylcyclopentanones **2a,b** and **3a,b** or their β -elimination products (**4** and **5**); but we were uncertain whether significant regio and stereoselectivity would be observed. An earlier study by Cheer and Johnson³ demonstrated an intriguing catalyst-specific selectivity in related rearrangements of a five-membered ring analog of **1**.



Epoxycyclobutanols **1a** to **1d** were prepared by epoxidation (MCPBA⁴) of vinylcyclobutanols **6** and **7**, which in turn were synthesized from bicyclo [4.2.0] octan-7-one (**8**) as shown in equation 1. The stereoselectivity of addition reactions to **8** (or its ethylidene derivative) is attributed to a folded configuration in which the convex face is less hindered than the concave face.



Diastereomers **1c** and **1d** were separated by flash chromatography⁵, but all our efforts to separate the equimolar mixture of **1a** and **1b** proved ineffective. Because of the difference in reactivity between **1a** and **1b** we were able to use this mixture of epimers for many of our studies. However, a pure sample of each isomer was eventually prepared from the corresponding bromohydrins, **9a** and **9b** respectively, by treatment with methanolic base. Similarly bromohydrin **9c** gave **1c** and its epimer (**9d**) gave **1d**.



We have examined acid-catalyzed rearrangements of **1a** through **1d** under different conditions with the results given in Table 1.

TABLE 1

Reactions of Stereoisomeric 7-Oxirylbicyclo [4.2.0] octan-7-ols **1a** through **1d**

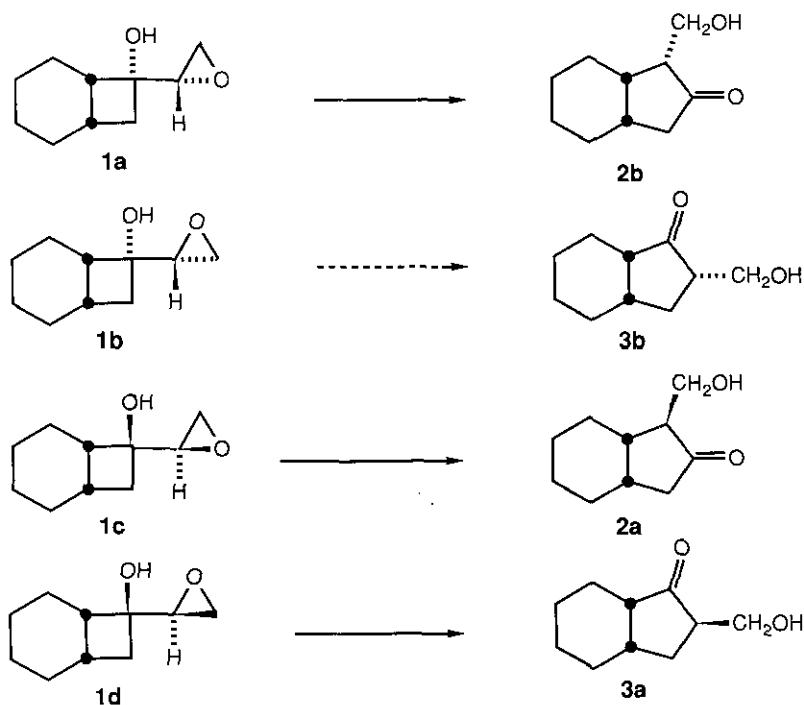
Reactant(s)	Conditions	Products (% Yield)
1a + 1b (1:1)	MgBr ₂ (1 eq.), THF, 25°C	9a (48) + 9b (48)
1c	"	9c (98)
1d	"	9d (98)
1a + 1b (1:1)	BF ₃ ·ether(cat.), CH ₂ Cl ₂ , -78°	2b (45) + 1b (43)
1c	BF ₃ ·ether(cat.), CH ₂ Cl ₂ , -17°	2a (74)
1d	"	3a (88)

Our interpretation and rationalization of these results was complicated by the fact that none of the key compounds (**1** through **5**) had been reported previously. Furthermore, although each of the diastereomers **1a** through **1d** exhibits a characteristic chemistry, the corresponding ¹H and ¹³C nmr spectra cannot be assigned unambiguously to specific configurations. Consequently, a series of chemical correlations and interconversions was undertaken, which led ultimately to the structural assignments presented in Scheme 1.

Epimeric ketols **2a** and **2b** were converted to enone **4**, either by acid-induced dehydration or by treatment of the derived mesylate with 1,5-diazabicyclo [5.4.0] undecene-5 (DBU). An independent synthesis of **4** was accomplished in poor yield by a Mannich reaction of *cis*-bicyclo [4.3.0] nonan-8-one⁶. Similarly β-elimination of **3a** gave enone **5**, easily distinguished from **4** by spectroscopy. The remaining isomeric ketol **3b** was neither obtained as a rearrangement product nor prepared in the course of this project. These conversions of ketols to enones clearly demonstrate the high regioselectivity of the rearrangements induced by mild treatment of **1a** through **1d** with boron trifluoride. Thus **1a** and **1c** undergo ring expansion with a shift of the bridgehead carbon, whereas **1d** rearranges by a shift of the methylene group. We are not yet able to explain the curious reluctance of **1b** to rearrange under these mild conditions. On more vigorous treatment (higher temperature and/or equimolar boron trifluoride) **1b** is transformed to an intractable mixture including polymeric products.

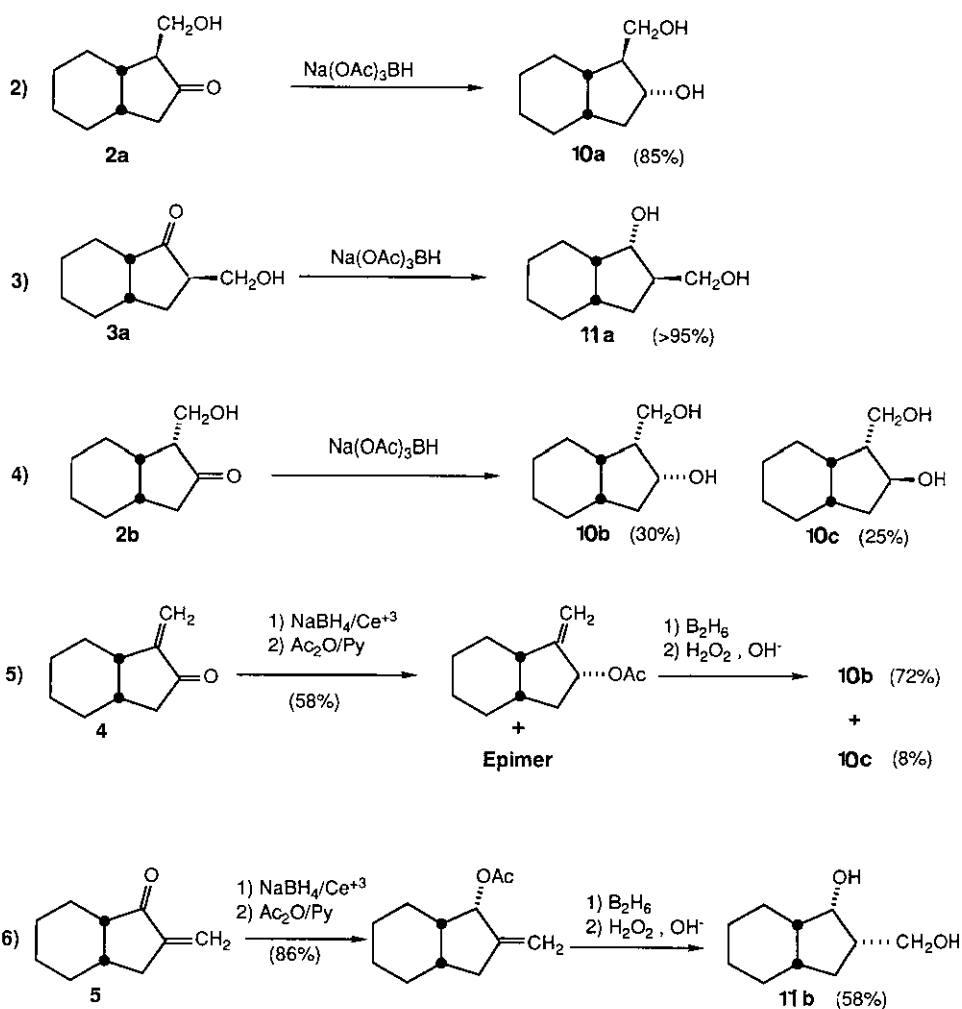
As a first step in rationalizing the selective behavior of isomers **1a** through **1d** in the boron trifluoride-catalyzed rearrangement, we made the plausible assumption that preferred transition states would have an anti-periplanar configuration of the oxirane CH-O bond and the migrating residue of the four-membered ring. Following a careful inspection of Dreiding molecular models, we arrived at the configurational relationships depicted in Scheme 1. We must emphasize that no other evidence for the configurations of the isomer pairs **1a** and **1b** or **1c** and **1d** yet exists. Nevertheless, these assignments result in a completely self-consistent and reasonable description of these remarkably selective reactions. Since the bromohydrins derived from the isomers of **1** are all crystalline, X ray analysis of these may provide support for our assignments. We have not yet obtained suitable single crystals.

SCHEME 1



Since the epimers of **2** and **3** could not be assigned firm configurations on the strength of their spectroscopic characteristics alone, we converted these β -ketols to 1,3-diols that we defined as *cis* or *trans* from the expected stereoselectivity of the reduction. These assignments were then checked by observing the relative rates of acetonide formation. For this purpose we used sodium triacetoxyborohydride, a highly-selective reducing agent, which reduces ketones only when a

neighboring hydroxyl group serves as a ligand for intramolecular delivery of hydride to the carbonyl function⁷. Of the three ketols obtained from the boron trifluoride-catalyzed rearrangements, both **2a** and **3a** have their hydroxymethyl groups projecting from the convex face of the *cis*-bicyclononane ring system. In these cases we expected the normal convex facial-selectivity of the reduction to be enhanced by the neighboring group effect. In the event, triacetoxyborohydride reduction of **2a** and **3a** gave high yields of a characteristic diol, which in each case is assigned the *trans* configuration (equations 2 and 3). On the other hand, isomer **2b** has a concave-face oriented hydroxymethyl group and the reduction proceeds at both faces of the molecule, albeit sluggishly. Both *cis* and *trans* diols are thus obtained (equation 4).



Alternative preparations of such diols from enones **4** and **5** were also explored (equations 5 and 6). A sequence of reactions beginning with carbonyl reduction and ending with hydroboration/oxidation was assumed to proceed predominantly at the less hindered convex face. Finally, **10a** was prepared from cis-bicyclo [4.3.0] nonan-8-one by a sequence of reactions (carboxymethylation followed by sodium borohydride reduction, dihydropyran protection, lithium aluminum hydride reduction and deprotection) which should give the trans configuration noted here.

The cis diols **10b** and **11b** form acetonide derivatives rapidly on treatment with anhydrous cupric sulfate in acetone solution (> 50% yield in 2 h at 25°C). The trans isomers **10a**, **10c** and **11a** reacted sluggishly, giving less than 5% acetonide under equivalent conditions.

EXPERIMENTAL

Melting points were determined on a Hoover-Thomas apparatus and are uncorrected. Flash chromatographic separations were achieved using Merck Silica Gel (230-400 mesh) under slight pressure, as described by Still et al.⁵. Infrared (IR) spectra were recorded on a Perkin-Elmer 237B grating spectrophotometer and calibrated with polystyrene. UV absorption spectra (in 95% EtOH) were measured with a Perkin-Elmer 200 spectrophotometer. ¹H nmr spectra and ¹³C nmr spectra were obtained on a Bruker 250 MHz spectrometer operating at 69.8 MHz for carbon. In both cases tetramethylsilane served as an internal standard and the samples were in deuteriochloroform solution unless stated otherwise. Mass spectra (MS) were obtained with a Finnigan 4000 GC/MS spectrometer and high resolution measurements were made on a JEOL JMS-HX 110 mass spectrometer. Microanalyses were performed by Spang Microanalytical Labs, Eagle Harbor, MI.

Bicyclo [4.2.0] octan-7-one **8**.

A solution of 8,8-dichlorobicyclo [4.2.0] octan-7-one (2.0 g, 10.4 mM), prepared by cycloaddition of dichloroketene to cyclohexene, in glacial acetic acid (25 ml) was cooled (ice bath) and stirred while zinc dust (2.5 g) was added in portions. The reaction mixture was raised to 75°C, stirred overnight and then filtered through Celite. The filtrate was mixed with ether, washed several times with cold water followed by aqueous sodium bicarbonate and dried (Na₂SO₄). Distillation of the crude product (Kugelrohr, 0.3 torr) gave **8**⁸ (1.15 g, 90%) having the following properties: IR 1780 cm⁻¹; ¹H nmr δ 3.27 (m, 1H), 3.13 (m, 1H), 2.50 (m, 1H), 2.44 (m, 1H), 2.15 (m, 1H), 1.95 (m, 1H), 1.10-1.80 (m, 6H) ppm.

Vinylcyclobutanol 6

To a stirred solution of the Grignard reagent prepared by treating vinyl bromide (7.7 ml, 108 mM) in THF (20 ml) with magnesium (3.18 g, 129 mM), was added a solution of cyclobutanone **8** (5.34 g, 43 mM) in THF (20 ml). This mixture was stirred at room temperature overnight, and then quenched by addition of saturated aqueous ammonium chloride. Extraction with ether, followed by conventional workup and Kugelrohr distillation (48-50°C, 0.25 torr) gave **6** (5.433 g, 83%)⁹: IR 3600-3450 cm^{-1} ; ^1H nmr δ 6.15 (dd, 1H, $J=10.7$ and 17.4 Hz), 5.25 (dd, 1H, $J=17.4$ and 1.2 Hz), 5.00 (dd, 1H, $J=10.7$ and 1.2 Hz), 0.84-2.10 (m, 13H) ppm; ^{13}C nmr δ 143.5, 111.0, 73.1, 42.5, 37.1, 25.9, 23.5, 22.6, 21.7, 21.5 ppm.

Vinylcyclobutanol 7

A mixture of ethyltriphenylphosphonium bromide (30 g, 81 mM) and 0.5M of *t*-AmOK in toluene (180 ml, 90 mM) was refluxed for 30 min; a solution of cyclobutanone **8** (2.55 g, 21 mM) in toluene (10 ml) was added dropwise, and this mixture was refluxed 3 h. After mixing with ice water, the resulting mixture was extracted with toluene and the extracts were washed with 10% aqueous HCl, saturated aqueous NaHCO_3 brine and dried over Na_2SO_4 .

To one-third of the ethylidenecyclobutane solution thus obtained was added 1.5 g of *m*-chloroperoxybenzoic acid (MCPBA) at room temperature. The progress of the reaction was followed by tlc and additional amounts of MCPBA were occasionally added in order to complete the reaction. The reaction was quenched with 10% aqueous Na_2SO_3 ; the organic layer was diluted with ether, washed with saturated aqueous Na_2CO_3 , and dried over Na_2SO_4 . Removal of the solvent and purification by flash chromatography gave a mixture of epoxides which was used immediately in the next step.

To a cold solution of *n*-butyl lithium in hexane (13 ml, 10.1 mM) was added a solution of diethylamine (2 ml, 21 mM) in ether (20 ml). Following a 30 min reaction period, an ether solution of the previous epoxide mixture was added, and this solution was then stirred at reflux for 2 h. The reaction was quenched with MeOH, diluted with ether and water and the organic layer was washed with cold 10% aqueous HCl, brine and dried over Na_2SO_4 . Evaporation of the solvent and chromatography using 3 : 1 pentane ether as eluent gave vinylcyclobutanol **6** (0.171 g, 16.4%) and vinylcyclobutanol **7** (0.363 g, 54.2%). Properties of **7**: IR 3300-3650 cm^{-1} ; ^1H nmr δ 6.09 (dd, 1H $J=10.7$ and 17 Hz), 5.23 (dd, 1H, $J=17$ and 1.5 Hz), 5.12 (dd, 1H, $J=10.7$ and 1.5 Hz), 2.62 (m, 1H), 2.42 (m, 1H), 1.92 (m, 1H), 0.78-1.88 (m, 9H) ppm; ^{13}C nmr δ 141.4, 113.2, 77.7, 44.2, 36.4, 26.9, 25.7, 23.2, 22.4, 22.0 ppm.

7-Oxirylbicyclo [4.2.0] octan-7-ols, 1a, 1b, 1c and 1d

Vinylcyclobutanols **6** and **7** were epoxidized by MCPBA using the same procedure. A solution of the substrate (1.0 g, 6.6 mM) in 20 ml of methylene chloride was cooled (ice bath) and treated with MCPBA (ca. 10 mM) by dropwise addition of a methylene chloride solution of the peracid. Following an overnight reaction period (25°C), the reaction mixture was filtered and the filtrate was washed with 10% aqueous sodium sulfite and brine. The dried solution yielded an oily product, which was purified by chromatography to give 1.05 g (95%) of an equimolar mixture of diastereomeric epoxycyclobutanols.

The mixture of **1c** and **1d** obtained from **7** was separated by chromatography. Characteristic properties of each isomer are: **1c** IR 3400-3650 cm^{-1} ; ^1H nmr δ 3.25 (m, 1H), 2.74 (m, 2H), 2.48 (m, 2H), 1.10-2.30 (m, 11H) ppm; ^{13}C nmr (acetone d_6) δ 75.5, 52.5, 43.3, 42.2, 33.2, 27.0, 26.1, 23.2, 22.8, 22.2 ppm. **1d** IR 3450-3600 cm^{-1} ; ^1H nmr δ 3.28 (dd, 1H, $J=4.1$ and 2.8 Hz), 2.85 (dd, 1H, $J=5.2$ and 2.8 Hz), 2.75 (dd, 1H, $J=5.2$ and 4.1 Hz), 2.60 (m, 1H), 2.36 (m, 1H), 2.20 (brs, 1H), 1.95 (ABq, 2H), 1.20-1.80 (m, 8H) ppm; ^{13}C nmr δ 76.5, 54.3, 44.2, 43.3, 34.1, 27.1, 25.7, 22.4, 22.3, 21.9 ppm. Microanalysis (C and H) supported the assigned structure.

Isomers **1a** and **1b** were prepared from the corresponding bromohydrins (**9a** and **9b**) after chromatographic separation, as described below. Characteristic properties are: **1a** IR 3500-3600 cm^{-1} ; ^1H nmr δ 3.21 (dd, 1H, $J=4.0$ and 2.9 Hz), 2.83 (dd, 1H, $J=5.0$ and 2.8 Hz), 2.78 (dd, 1H, $J=5.0$ and 4.0 Hz), 1.0-2.5 (m, 13H) ppm; ^{13}C nmr δ 70.7, 56.7, 44.4, 39.5, 36.1, 26.1, 24.3, 24.2, 21.7, 21.1 ppm. **1b** IR 3500-3550 cm^{-1} ; ^1H nmr δ 3.27 (dd, 1H, $J=2.5$ and 5.0 Hz), 2.82 (dd, 1H, $J=2.5$ and 5.0 Hz), 2.77 (dd, 1H, $J=5.0$ and 5.0 Hz), 2.35 (m, 1H), 0.8-2.2 (m, 12H) ppm; ^{13}C nmr δ 71.5, 56.8, 44.1, 40.0, 35.1, 27.0, 24.8, 23.3, 22.4, 21.9 ppm. Microanalysis supported the assigned structures.

Preparation of Bromohydrins 9a, 9b, 9c and 9d.

A solution of an epoxycyclobutanol isomer, **1abcd**, (0.33 g, 2.0 mM) in 10 ml of THF was stirred at room temperature while magnesium bromide etherate (0.68 g) was added. Thirty minutes later the reaction mixture was quenched with water and carefully acidified by the addition of 1N hydrochloric acid. Ether extraction in the usual manner gave crude bromohydrin which was purified by chromatography (pentane:ether/3:1). From a 1:1 mixture of **1a** and **1b** the respective bromohydrins (**9a** and **9b**) were obtained in 46% yield each, after separation. The other isomers (**9c** and **9d**) were obtained from **1c** and **1d** respectively in > 95% yield. **9a** mp 110-112°C; IR 3550 cm^{-1} ; ^1H nmr δ 3.88 (m, 1H), 3.62 (dd, 1H, $J=2.3$ and 10.6 Hz), 3.49 (dd, 1H, $J=9.6$ and 10.6 Hz), 1.03-2.51 (m,

14H) ppm; ^{13}C nmr δ 76.2, 75.8, 39.6, 37.6, 35.5, 27.3, 24.8, 23.2, 22.2, 20.8 ppm. **9b** mp 142-143°C; IR 3550 cm^{-1} ; ^1H nmr δ 3.51 (dd, 1H, $J=10.1$ and 10.7 Hz), 3.91 (dd, 1H, $J=2.3$ and 10.1 Hz), 3.65 (dd, 1H, $J=2.3$ and 10.7 Hz), 1.80-2.63 (m, 8H), 0.93-1.80 (m, 6H) ppm; ^{13}C nmr ($\text{DMSO}-d_6$) δ 76.8, 75.6, 38.2, 37.0, 35.9, 27.0, 24.8, 22.0, 21.4, 21.1 ppm. **9c** mp 138-140°C; IR 3400-3650 cm^{-1} ; ^1H nmr δ 3.92 (dd, 1H, $J=2.9$ and 9.3 Hz), 3.50 (dd, 1H, $J=9.3$ and 10.8 Hz), 3.43 (dd, 1H, $J=2.9$ and 10.8 Hz), 2.72 (m, 1H), 1.0-2.5 (m, 13H) ppm; ^{13}C nmr (acetone- d_6) δ 78.9, 76.2, 43.0, 36.9, 36.7, 27.3, 26.8, 23.5, 23.1, 22.1 ppm. **9d** mp 97-98°C; IR 3400-3600 cm^{-1} ; ^1H nmr δ 3.97 (dd, 1H, $J=4.8$ and 7.6 Hz), 3.47 (m, 2H), 2.70 (m, 1H), 2.40 (brs, 2H), 2.18 (m, 1H), 1.0-1.9 (m, 10H) ppm; ^{13}C nmr (acetone- d_6) δ 78.5, 75.0, 44.8, 36.3, 34.3, 26.8, 23.5, 23.1, 22.2, 22.0 ppm.

Base-Induced Cyclization of Bromohydrins 9 to Epoxycyclobutanols 1

A stirred solution of bromohydrin **9a** (95 mg, 0.38 mM) in methanol (5 ml) was treated with 0.4 ml of 1N sodium hydroxide in methanol. After 24 h the reaction mixture was neutralized with dilute aqueous hydrochloric acid and diluted with ether. The organic layer was washed and dried; removal of the solvent gave 63 mg (98%) of **1a**. In a similar reaction **9b** gave **1b** in 75% yield.

Boron Trifluoride-Catalyzed Rearrangement of 1.

The following procedure is typical. To a stirred solution of **1a** and **1b** (0.33 g, 2.0 mM) in methylene chloride (10 ml), cooled to -78°C , was added ca. 0.2 mM of boron trifluoride etherate. This mixture was stirred for 90 min, quenched with water and mixed with more methylene chloride. The organic layer was washed (aq. bicarbonate and brine), dried and concentrated. Chromatography of the product gave **2b** (0.15 g, 43%) and recovered **1b** (0.16 g, 43%).

Characteristic properties of the rearranged hydroxymethyl ketones from **1a**, **1c** and **1d** are: **2b** IR 3300-3600, 1725 cm^{-1} ; ^1H nmr δ 3.90 (dd, 1H, $J=7.4$ and 11.2 Hz), 3.62 (dd, 1H, $J=6.9$ and 11.2 Hz), 2.59 (m, 1H), 2.05-2.50 (m, 5H), 0.80-1.80 (m, 8H) ppm; ^{13}C nmr δ 221.3, 58.9, 58.3, 38.6, 38.2, 33.3, 26.2, 24.5, 23.4, 19.8 ppm. **2a** IR 3450-3600, 1725 cm^{-1} ; ^1H nmr δ 3.79 (dd, 1H, $J=11.1$ and 4.3 Hz), 3.59 (dd, 1H, $J=11.1$ and 6.1 Hz), 2.10-2.51 (m, 6H), 0.85-1.80 (m, 8H) ppm; ^{13}C nmr δ 222.3, 60.5, 50.4, 45.8, 36.7, 33.7, 28.5, 25.6, 24.3, 20.4 ppm. **3a** IR 3350-3600, 1725 cm^{-1} ; ^1H nmr δ 3.84 (dd, 1H, $J=10.8$ and 5.2 Hz), 3.67 (dd, 1H, $J=10.8$ and 6.4 Hz), 0.85-2.59 (m, 14H); ^{13}C nmr δ 222.3, 62.9, 50.4, 47.6, 34.9, 29.5, 29.1, 24.4, 22.9, 22.7 ppm. All these isomers displayed a weak molecular ion at m/e 168 in their mass spectra.

Unsaturated Ketones 4 and 5.

Ketol 2a was converted to a mesylate derivative (>90%) by treatment with methane-sulfonyl chloride in triethyl amine/methylene chloride solution at 0°C. The purified mesylate in ether solution (0°C) was reacted with DBU for 2 h. Chromatography of the crude product gave 4 in 78% overall yield.

Ketol 2b gave 4 in 75% yield directly by mixing with a suspension of Dowex 50x8-100 acidic ion exchange resin in chloroform.

4 : IR 1720 and 1635 cm^{-1} ; ^1H nmr δ 6.15 (d, 1H, J=3 Hz), 5.15 (dd, 1H, J=3 and 1 Hz), 0.85-2.40 (m, 12H) ppm; ^{13}C nmr δ 207.0, 146.8, 115.8, 44.1, 40.8, 33.3, 28.5, 25.8, 23.7, 20.4 ppm; UV λ_{max} (EtOH) 236 nm; MS m/e 150 (mol. ion), 108 (base).

Ketol 3a was converted to a mesylate derivative (>95%) and eliminated by DBU treatment as above. Chromatography of the crude product gave 5 in 94% overall yield.

5 : IR 1720 and 1645 cm^{-1} ; ^1H nmr δ 6.04 (m, 1H), 5.30 (m, 1H), 2.62 (m, 1H), 0.8-2.5 (m, 11H) ppm; ^{13}C nmr δ 207.5, 145.2, 119.2, 49.5, 35.8, 34.3, 30.5, 25.5, 24.0, 23.5 ppm; UV λ_{max} (EtOH) 235 nm; MS m/e 150 (mol. ion), 40 (base).

Reduction of Ketols 2 and 3 to Diols 10 and 11.

The following is a typical procedure. Sodium borohydride (0.2 g, 5.1 mM) was added portionwise to chilled glacial acetic acid (15°C) and stirred until gas evolution ceased. Ketol 3a (73 mg, 0.4 mM) was added, and this mixture was stirred at room temperature for 4 h. Following a water quench and ether extraction, the crude product was chromatographed and yielded 11a (99%). The properties of this and related diols are: 10a IR 3500-3600 cm^{-1} ; ^1H nmr δ 4.07 (ddd, 1H, J=8.3, 5.7 and 2.5 Hz), 3.75 (dd, 1H, J=10.4 and 4.9 Hz), 3.43 (dd, 1H, J=10.4 and 9 Hz), 3.06 (bbs, 2H), 1.10-2.12 (m, 13H) ppm; ^{13}C nmr δ 77.6, 65.2, 52.2, 39.7, 39.5, 36.8, 29.1, 26.9, 24.1, 22.5 ppm. 10b mp 68-69°C; IR 3500-3550 cm^{-1} ; ^1H nmr δ 4.23 (m, 1H), 3.82 (dd, 1H, J=10.1 and 6.2 Hz), 3.71 (dd, 1H, J=10.1 and 9 Hz), 2.90 (bbs, 2H), 0.80-2.20 (m, 13H) ppm; ^{13}C nmr (acetone- d_6) δ 73.0, 59.7, 52.4, 41.3, 38.6, 38.3, 27.5, 26.4, 24.3, 21.5 ppm. 10c mp 110-112°C; IR 3500-3600 cm^{-1} ; ^1H nmr δ 4.24 (m, 1H), 3.83 (m, 1H), 3.71 (dd, 1H, J=10 and 9 Hz), 1.83-2.38 (m, 6H), 0.75-1.75 (m, 9H) ppm; ^{13}C nmr (acetone- d_6) δ 75.2, 62.1, 57.3, 41.4, 37.5, 37.2, 27.5, 25.9, 24.0, 24.1 ppm. 11a mp 78-80°C; IR 3500-3600 cm^{-1} ; ^1H nmr δ 4.00 (dd, 1H, J=5.7 and 2.1 Hz), 3.80 (dd, 1H, J=5.7 and 4.4 Hz), 3.63 (dd, 1H, J=8.0 and 8.7 Hz), 1.1-2.30 (m, 15H) ppm; ^{13}C nmr δ 80.1, 67.1, 45.8, 43.9, 34.4, 27.7, 26.9, 24.6, 22.0, 21.0 ppm.

Preparation of 11b from Enone 5.

Enone 5 (0.35 g, 2.34 mM) was reduced in cold (ice bath) methanol solution containing cerium (III) chloride (2.4 mM) and sodium borohydride (3 mM). The resulting allylic alcohol (88%) was separated from its epimer (7%) by chromatography, and then converted to an acetate derivative (acetic anhydride in pyridine solution). To a solution of 63 mg (0.32 mM) of this acetate in THF was added 1 ml of a 1M solution of diborane in THF. After 3 h this reaction was treated with 30% hydrogen peroxide (3 ml) and base (4 ml of 10% sodium hydroxide). Following workup, the crude product was chromatographed to give **11b** (32 mg, 58%) IR 3400-3600 cm^{-1} ; ^1H nmr 4.42 (m, 1H), 3.76 (m, 2H), 1.90-2.50 (m, 7H), 1.0-1.8 (m, 8H) ppm; ^{13}C nmr δ 77.6, 64.2, 43.6, 44.4, 35.7, 29.6, 27.9, 27.5, 22.0, 21.8 ppm.

Conversion of Diols 10 and 11 to Acetonide Derivatives.

The following is a typical procedure. A solution of diol **11b** (79.6 mg, 0.47 mM) in dry acetone (10 ml) was mixed with anhydrous copper sulfate (200 mg) and stirred at room temperature for 2 h. Filtration and chromatography of the crude product from the filtrate resulted in some loss of the volatile acetonide. In this case recovered **11b** amounted to 7 mg (9%) and the acetonide yield was 43 mg (44%). **Acetonide of 11b**: ^1H nmr δ 4.07 (dd, 1H, $J=5.2$ and 5.2 Hz), 3.87 (dd, 1H, $J=11.3$ and 5.2 Hz), 3.48 (dd, 1H, $J=11.3$ and 5.8 Hz), 1.32 (s, 3H), 1.27 (s, 3H), 0.9-2.0 (m, 13H) ppm; ^{13}C nmr δ 98.4, 75.5, 62.4, 43.0, 38.5, 37.1, 33.1, 30.6, 28.2, 24.0, 23.7, 21.2 ppm. **Acetonide of 10b** (52% yield): ^1H nmr δ 4.24 (m, 1H), 3.84 (dd, 1H, $J=7.0$ and 11.7 Hz), 3.74 (dd, 1H, $J=6.4$ and 11.7 Hz), 1.32 (s, 3H), 1.26 (s, 3H), 1.0-2.0 (m, 13H) ppm; ^{13}C nmr δ 98.0, 71.2, 58.8, 43.3, 41.1, 37.0, 34.7, 26.9, 26.4, 25.7, 24.6, 21.4, 20.7 ppm.

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