A Facile Access to Densely Functionalized Substituted Cyclopentanes and Spiro Cyclopentanes. Carbocation Stabilization Directed Bond Migration in Rearrangement of Cyclobutanes

Azizul Haque,† Anjan Ghatak,† Subrata Ghosh,*,† and Nanda Ghoshal‡

Department of Organic Chemistry, Indian Association for the Cultivation of Science, Jadavpur, Calcutta 700 032, India, and Medicinal Chemistry Division, Indian Institute of Chemical Biology, Jadavpur, Calcutta 700 032, India

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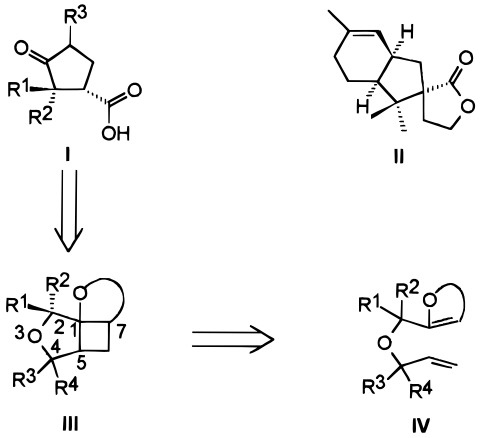
Substituted cyclopentanes are widely represented in nature and have served as valuable precursors[1] in the total synthesis of natural products. The cyclopentanone **I** having substituents at the 2, 3, and 5 positions as present in the novel sesquiterpene herbadysidolide **II**[2] and related compounds poses considerable synthetic challenge. Although much effort has been spent on annulation of cyclopentane rings[3] onto preexisting rings, little attention has been given to the synthesis of cyclopentanones[4] with multiple substitution as represented by the structure **I**. Construction of cyclopentanones of this type through stepwise addition of substituents to prebuilt cyclopentanone is a lengthy process and is in general attended with poor regio- and stereoselectivity. An approach in which substituents are directly generated during construction of the cyclopentane ring is likely to have great synthetic importance in terms of selectivity and step economy. Development of a general methodology to construct cyclopentanones represented by the general structure **I**, thus, became our primary objective.

We anticipate that acid-induced rearrangement[5] of the cyclobutane ring in the tricyclic compound **III** (R^3,R^4 = O) may produce the desired cyclopentanone **I** provided 1,5-bond migration takes place preferentially over the 1,7-bond. In light of the stereoelectronic requirement[6] in the pinacol rearrangement, the 1,7-bond migration may be competitive. Thus it is of considerable interest to investigate the rearrangement of the cyclobutane derivatives **III** leading to a general route for the direct synthesis of cyclopentanones with functionalised substituents.



Results and Discussion

It appeared to us that an intramolecular [2 + 2] photocycloaddition of the diene **IV** (R^3,R^4 = O) would be the most straightforward route to the cyclobutanes **III** (R^3,R^4 = O). Although the diallyl ether **1a** undergoes smooth copper(I) catalyzed photocycloaddition[7] to produce **2a**, relating to another synthetic program, we have noted[8] that the allyl ester **1b** failed to undergo photocycloaddition to produce **2b** under sensitized or catalyzed conditions. We believe that the failure of **1b** to undergo cycloaddition is possibly due to the inability of the diene **1b** to adopt the requisite conformation for cycloaddition. Thus, in the present investigation we decided to use the cyclobutane derivatives **III** (R^3 = R^4 = H).

a: R^1=R^2=H, R^3=CH_2OH
b: R^1, R^2=O, R^3=Me

The preparation of the dienes and their photocycloaddition were carried out according to Scheme 1 and are illustrated with the transformation of acetone **3a** to the photoadduct **6a**. Reaction of acetone **3a** with (dihydrofuryl)lithium afforded the carbinol **4a** in 71% yield. Coupling of the carbinol **4a** with allyl bromide afforded the diene **5a** in 80% yield. The diene **5a** was easily identified by its ^{1}H NMR spectral data. Irradiation of the diene **5a** in a diethyl ether solution in the presence of CuOTf as catalyst according to the procedure of Salomon[7] afforded the bis tetrahydrofuran cyclobutane **6a** in 50% yield after chromatographic purification. The disappearance of the olefinic protons of the starting diene **5a** in the ^{1}H NMR spectrum of the product is a clear indication of the cycloaddition. Further, the presence of two Me singlets at δ 1.13 and 1.18, two one-proton quartets at δ 2.5 (J = 6 Hz) and 2.85 (J = 6 Hz) assigned to the C_7 and C_5 methine protons, and the resonance at δ 3.66 (1H, d, J = 10 Hz), 3.84−4.03 (2H, m), and 4.20 (1H, t, J = 7.5 Hz) for the oxomethylene protons indicated the identity of the structure **6a**. This structural assignment is corroborated by ^{13}C NMR (DEPT) spectral data showing two Me's at δ 20.1 and 20.6, two methine carbons at δ 36.4 and 40.4, the OCH_2 of the tetrahydrofuran at δ

† Indian Association for the Cultivation of Science.
‡ Indian Institute of Chemical Biology.

(1) For example see. (a) Stork, G.; Saccomano, N. A. *Tetrahedron Lett.* **1987**, *28*, 2087. (b) Mehta, G.; Krishnamurthy, N.; Karra, S. R. *J. Am. Chem. Soc.* **1991**, *113*, 5765. (c) Ho, T. L.; Liang, F. S. *J. Chem. Soc., Chem. Commun.* **1996**, 1887.

(2) Faulkner, D. J. *Nat. Prod. Rep.* **1995**, *12*, 223. (b) Schram, T. J.; Cardellira, J. H., II. *J. Org. Chem.* **1985**, *50*, 4155.

(3) Ramaiah, M. *Synthesis* **1984**, 529. (b) Paquette, L. A. *Top. Curr. Chem.* **1984**, *119*, 1. (c) Little, R. D. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, 1991; Vol. 5, p 239. (d) Habermas, K. L.; Denmark, S. E. *Org. React.* **1994**, *45*, 1.

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(5) For pinacol type rearrangement of cyclobutane derivatives to form cyclopentanones see: (a) Ikeda, M.; Takahashi, M.; Uchini, T.; Ohno, K.; Tamura, Y.; Kido, M. *J. Org. Chem.* **1983**, *48*, 4241. (b) Moriarty, K. J.; Shen, C. C.; Paquette, L. A. *Synlett* **1990**, 263. (c) Jamart-Gregoire, B.; Brosse, N.; Ianelli, S.; Nardelli, M.; Caubere, P. *Tetrahedron Lett.* **1991**, *32*, 3069. (d) Nath, A.; Venkateswaran, R. V. *J. Chem. Soc., Chem. Commun.* **1993**, 281.

(6) Mundy, B. P.; Otzenbenger, R. D. *J. Chem. Educ.* **1971**, *48*, 431.

(7) Ghosh, S.; Raychaudhuri, S. R.; Salomon, R. G. *J. Org. Chem.* **1987**, *52*, 83.

(8) Ghosh, S.; Sarkar, S. Unpublished result.

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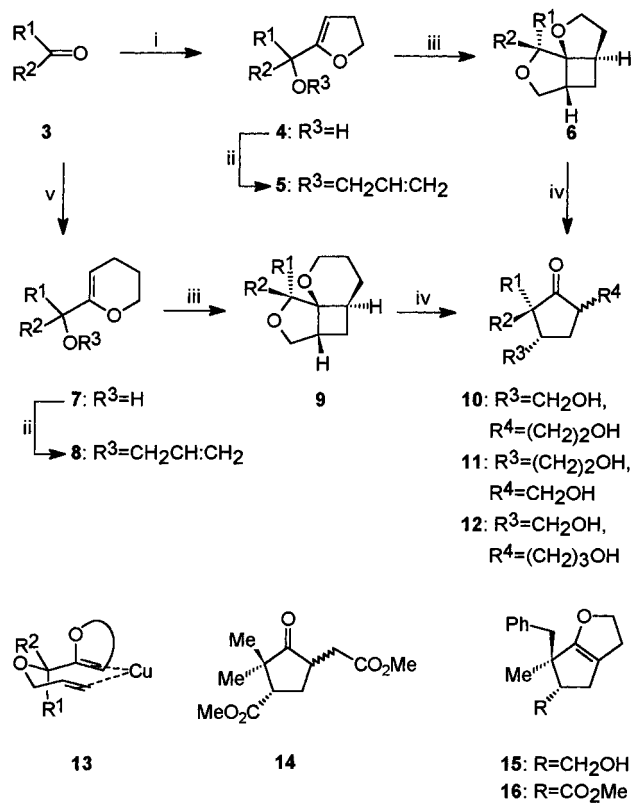
Scheme 1[a]



a: R^1=R^2=Me; **b**: R^1=Me, R^2=CH_2CH_2Ph; **c**: R^1=Me, R^2=CH_2Ph; **d**: R^1,R^2= -$(CH_2)_4$- ; **e**: R^1,R^2= -$(CH_2)_5$-

[a] Reagents: i, 2,3-dihydrofuran, THF, *t*-BuLi, −70 °C. ii, NaH, THF−HMPA, allyl bromide, reflux. iii, *hν*, CuOTf, Et_2O. iv, TfOH−TFA, 50−55 °C, 1 h, then NaOH−H_2O, reflux. v, 3,4-dihydropyran, THF, *t*-BuLi, −70 °C.

Table 1. Synthesis of Cyclopentanes

entry	ketones	dienes (% yield)	photoadducts (% yield)		cyclopentanes (% yield)[b]
1	**3a**	**5a** (57)	**6a** (50)		**10a** (55)
2	**3b**	**5b** (63)	**6b** (59)	5.3:1[a]	**10b** (58)
3	**3c**	**5c** (55)	**6c** (70)	>99.1[a]	**15** (60)
4	**3a**	**8a** (57)	**9a** (46)		**12a** (58)
5	**3b**	**8b** (66)	**9b** (45)	7.6:1[a]	**12b** (67)
6	**3c**	**8c** (56)	**9c** (40)	>99:1[a]	**12c** (57)
7	**3d**	**5d** (48)	**6d** (45)		**10d** (50)
8	**3e**	**5e** (62)	**6e** (60)		**10e** (58)
9	**3d**	**8d** (50)	**9d** (58)		**12d** (50)
10	**3e**	**8e** (55)	**9e** (57)		**12e** (67)

[a] Represents ratio of the two diastereoisomers. [b] Cyclopentanones obtained in each case were mixture of the diastereoisomers epimeric at C_5 in about 2.5:1 ratio.

68.3 and 70.5, and the quaternary carbons of the tetrahydrofuran at δ 78.4 and 96.4 in addition to cyclobutane methylene at δ 25.9 and the C_8-methylene at δ 31.7. Following the above sequence, the unsymmetrical ketones **3b** and **3c** were transformed to the cyclobutanes **6b** and **6c** through the dienes **5b** and **5c**, respectively. The results are summarized in Table 1. As expected, the diene **5b** produced a mixture of the photoadduct **6b** along with its C_2-diasteroisomer in a 4:1 ratio. The gross structures of the photoadducts were evident from their ^{1}H and ^{13}C NMR spectra, which are closely comparable to those of the cyclobutane derivative **6a**. The stereochemical assignment to the major component as **6b** followed from its formation through cycloaddition of the less sterically crowded Cu-complexed diene **13**[7] in which CH_2CH_2Ph group, bulkier than Me, occupied an exo position. In accord with this stereochemical outcome in photocycloaddition, the diene **5c** in which the CH_2CH_2-Ph group has been replaced by the more bulkier CH_2Ph group produced mainly the photoadduct **6c** in 70% yield.

A second series of cyclobutane derivatives (**9a**−**c**) was also prepared for this investigation. The ketones **3a**−**c** were transformed to the dienes **8a**−**c** by reaction with (dihydropyranyl)lithium followed by coupling of the resulting carbinols **7a**−**c** with allyl bromide. Photocycloaddition of these dienes (**8a**−**c**) produced the cycloadducts **9a**−**c** with stereochemical outcome (Table 1) more or less identical to that observed for cycloaddition of the dienes **5a**−**c** prepared from dihydrofuran.

After the cyclobutane derivatives were successfully prepared, they were subjected to acid induced rearrangement. Rearrangement was found to take place very efficiently when a solution of the cyclobutane derivatives in trifluoroacetic acid (TFA) was heated with a catalytic quantity of trifluoromethane sulfonic acid (TfOH) at 50−55 °C for about an hour. The results are summarized in Table 1. The cyclobutane derivative **6a** produced a mixture of only two cyclopentanone derivatives in 3:1 ratio. A ^{13}C NMR spectrum of the major component in the mixture revealed the presence of two Me's at δ 18.2 and 24.5, two hydroxy methylene units at 61 and 63, two methines at 46.3 and 47.6, a quaternary center at 47.2, and a trisubstituted cyclopentanone at 225.5. Jones oxidation of this product followed by diazomethane treatment produced a mixture of the diesters in a 3:1 ratio as indicated by ^{1}H NMR. NMR spectral data combined with its transformation to the diesters indicated the product to be either a mixture of the regioisomers **10a** and **11a** or a mixture of the stereoisomers resulting from epimerization of either of the regioisomers. NMR spectral data were inadequate to differentiate between these two possibilities. The mass spectrum of the product mixture showed the base peak at *m/e* 142. This peak can be attributed to loss of CH_3CHO through McLafferty fragmentation from the regioisomer **10a** only. Thus, the product obtained from rearrangement of the cyclobutane derivative **6a** was a mixture of the two diastereoisomers **10a** resulting from epimerization at C_5 and rearrangement of the cyclobutane derivative **6a** has involved migration of 1,5-bond.

Structural assignment to the rearrangement product gets additional support from rearrangement of the cyclobutane derivative **6c** to produce, instead of the diol **10c**, a single compound, devoid of any carbonyl group (IR and ^{13}C NMR). Jones oxidation of this product followed by diazomethane treatment to produce a monoester instead of the expected diester corresponding to the diol **10c**, combined with ^{13}C NMR spectral data (two oxomethylene units at δ 64.0 and 69.4 and two quaternary olefinic carbons at δ 104.3 and 146.5 in addition to the aromatic carbons), dictated the cyclic enol ether structures **15** and **16** for the rearrangement product and the monoester, respectively. The stereochemical assignment to the rearrangement product **15** was based on the carbon chemical shift of the Me group. In general, in vicinally substituted cyclopentane derivatives, the Me group syn to the vicinal substituent is shielded by ~5 ppm over the one having with an anti Me[9] due to steric interaction of

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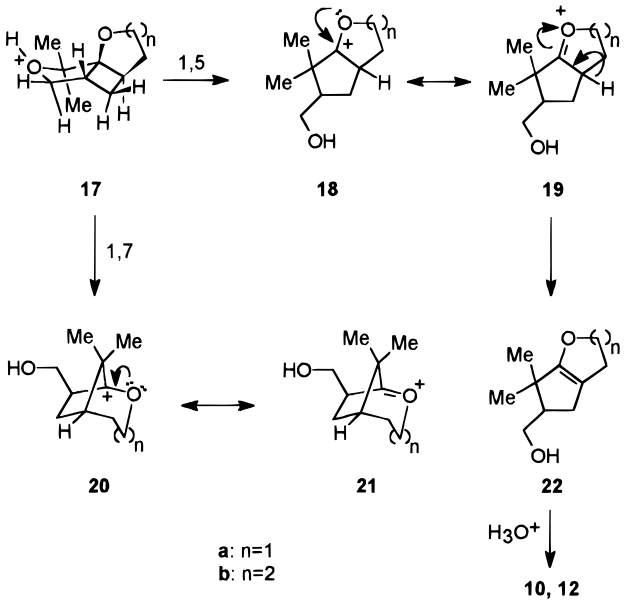
Scheme 2



the syn vicinal substituents. Thus, in the cyclopentanone **10a**, the two Me groups absorbed at δ 18.0 (syn Me) and 24.5 (anti Me). The chemical shift (15.4 ppm) of the Me carbon observed in the ^{13}C NMR of cyclopentane **15** is comparable to that of the syn Me of **10a**. This confirms that Me and CH_2OH are syn to each other in cyclopentane **15**.

The cyclobutane derivatives **6b** and **9a**−**c**, under the above condition, produced a mixture of cyclopentanones in each case (Table 1). The structural assignments of the cyclopentanones are based on a spectral data comparison with the cyclopentanone **6a**. The syn orientation of the Me and CH_2OH in each of them was ensured from the chemical shifts of the Me carbons (17.8−18.5 ppm). The cyclopentanone **9a** contains all of the requisite substituents and functionalities for elaboration to herbadysidolide.

The present methodology offers an excellent route for the synthesis of spiro cyclopentanones.[10] Thus in a similar fashion cyclopentanone **3d** and cyclohexanone **3e** provided the spiro cyclopentanones **10d**,**e** and **12d**,**e**.

The most remarkable feature in the rearrangement of the cyclobutane derivatives **6** and **9** was the selectivity observed in the migration of the 1,5-bond over the 1,7-bond. In light of the stereoelectronic requirement[6] in a pinacol type rearrangement, antiperiplanarity of the migrating bond with the bond to be broken is necessary. Molecular mechanics calculated[11] energy minimized conformation of the oxonium ions **17**, formed through protonation of the bis tetrahydrofuran derivatives **6** and **9** (Scheme 2) having energies of 58.1 and 61.0 kcal mol^{-1} for **17a** and **17b**, respectively, reveals that it is the 1,7-bond that meets this criterion. Hence, migration of the 1,7-bond would be preferred over that of the 1,5-bond if the reaction course is governed by a stereoelectronic factor. This unusual selectivity in 1,5-bond migration is attributed to be the result of the relative stabilities of the cations **18** and **20** formed by migration of the 1,5- and 1,7-bond, respectively, from the protonated species **17**. The cation **18** obtained by migration of the 1,5-bond can be stabilized through resonance with the structure **19**. On the other hand, the cation **20**, formed through migration of the 1,7-bond, cannot be stabilized by resonance with the structure **21** as its formation requires generation of a bridgehead double bond. Molecular mechanics calculation reveals that the cation **18a**, having an energy of 20.07 kcal mol^{-1}, is indeed stabilized by 10 kcal mol^{-1} over cation **20a**, having an energy of 30.26 kcal mol^{-1}. Similarly the cation **18b** (energy 24.76 kcal mol^{-1}) is stabilized by ~12 kcal mol^{-1} over cation **20b** (energy 36.15 kcal mol^{-1}). Thus in the present case stabilization of the intermediate carbocation overrides the stereoelectronic effect, resulting in exclusive migration of a stereoelectronically disfavored bond. Loss of a proton from the carbocation **19** then produces the cyclic enol ether **22**. The latter during aqueous workup undergoes hydrolysis to produce the cyclopentanones **10** and **12**. The isolation of the enol ether **15** from rearrangement of the cyclobutane derivative **6c** is in agreement with this rationalization. The failure of the enol ether **15** to undergo hydrolysis to produce the corresponding cyclopentanone **10c** is possibly due to destabilization of the latter arising from 1,3-eclipsing interaction between the bulkier C_2-benzyl and C_5-alkyl substituents. The strain arising through 1,3-eclipsing interaction is significantly relieved through enolization which is further facilitated by ring closure to form the very stable 5-membered ring.

In conclusion, this investigation has offered an excellent route for direct synthesis of substituted cyclopentanones and spiro cyclopentanones in which the substituents are functionalized for further elaboration. The synthesis had involved rearrangement of appropriately constructed cyclobutane derivatives. The stability of the carbonium ion formed after cyclobutane bond migration dictated the reaction course during rearrangement.

Experimental Section

Boiling points reported are uncorrected. The organic extracts were dried over anhydrous Na_2SO_4 unless otherwise stated. Column chromatography was performed on silica gel (60−120 mesh). Petroleum refers to the fraction of petroleum ether boiling in the range 60−80 °C. FT IR spectra were recorded neat. ^1H NMR spectra were recorded at 60 MHz in CCl_4 and at 200 MHz in a $CDCl_3$ solution. ^{13}C NMR spectra were recorded at 50 MHz in a $CDCl_3$ solution. Mass spectra were recorded at 70 eV. Elemental analyses[12] were performed in the microanalytical laboratory of this institute.

The general experimental procedure involved in the synthesis of cyclopentanones from carbonyl compounds is illustrated by the synthesis of the cyclopentanone **10a** from acetone.

Synthesis of the Diene. 5-(1′-(Allyloxy)-1′-methylethyl)2,3-dihydrofuran (5a). To a magnetically stirred solution of 2,3-dihydrofuran (3.4 mL, 45 mmol) in anhydrous THF (20 mL) under an argon atmosphere was added *t*-BuLi (20 mL, 30 mmol, 1.7 M in pentane) dropwise. After complete addition, the bath temperature was slowly raised to −10 °C (45 min) and the solution was stirred for 1 h at that temperature. The reaction mixture was again cooled to −78 °C. A solution of the ketone

(10) For a comprehensive account of synthetic approaches to spiro cyclopentanones, see: (i) Heathcock, C. H.; Graham, S. L.; Pirrung, M. C.; Plavac, F.; White, C. T. *The Total Synthesis of Sesquiterpenes*; ApSimon, J., Ed.; Wiley: New York, 1983; Vol. 5, pp 264−313. (ii) Vandewalle, M.; Clercq, P. D. *Tetrahedron* **1985**, *41*, 1767. (b) For recent approaches, see: Patra, D.; Ghosh, S. *J. Chem. Soc., Perkin Trans. 1* **1995**, 2635 and references cited therein.

(11) The minimum energy conformations of the cations **17a**,**b** were modeled using HyperChem Release 3 for Windows, a product of Autodesk Inc. The energy optimization of the structures were carried out using simulated annealing. Molecular mechanics calculations using MM+ force field were used for energy minimization.

(12) Satisfactory microanalytical data (C, H) were obtained for all compounds except the carbinols **4** and **7** and the dienes **5** and **8** which on attempted purification through chromatography or distillation underwent extensive decomposition.

3a (2.25 mL, 49 mmol) in THF (10 mL) was then added dropwise. After complete addition, the bath temperature was slowly raised to rt and stirring was continued for 1 h. The reaction mixture was then cooled to −20 °C and quenched by addition of a saturated aqueous NH_4Cl solution (10 mL). The reaction mixture was then extracted with ether (3 × 20 mL). The ether extract after drying (K_2CO_3) was concentrated. The residual oil was distilled to afford **4a** (2.7g, 71%): bp 60−65 °C (20 mm); ^{1}H NMR (60 MHz) δ 1.3 (6H, s), 2.15−2.81 (3H, m), 4.28 (2H, t, J = 9 Hz), 4.63 (1H, t, J = 3 Hz). The carbinol obtained as such was immediately transformed to the diene **5a** using the following procedure.

To a magnetically stirred suspension of NaH (670 mg, 11.2 mmol, 40% suspension in oil) in THF (35 mL) at rt under an N_2 atmosphere was added a solution of the carbinol **4a** (1g, 7.8 mmol) in THF (10 mL). After complete addition, the reaction mixture was heated under reflux for 2 h and then cooled to 50 °C. HMPA (9 mL) was then added followed by addition of allyl bromide (944 mg, 7.8 mmol) at a rate to maintain a mild reflux of THF. The reaction mixture was then refluxed for 2 h, cooled to rt and quenched by addition of water (20 mL). Finally, it was extracted with ether (3 × 30 mL). The ether extract after drying (K_2CO_3) was concentrated. The residual liquid, stabilized by addition of 1% NEt_3, was distilled to afford the diene **5a** (1.07 g, 80%): bp 70−72 °C (2 mm); ^{1}H NMR (60 MHz) δ 1.35 (6H, s), 2.61 (2H, dt, J = 3 and 9 Hz), 3.81 (2H, dt, J = 1 and 5 Hz), 4.33 (2H, t, J = 10 Hz), 4.73 (1H, t, J = 3 Hz), 4.86−6.20 (3H, m).

Irradiation of the Diene 5a. Synthesis of 2,2-Dimethyl-3,10-dioxatricyclo[5.3.0^{1,5}.0^{1,7}]decane (6a). A magnetically stirred solution of the diene **5a** (1.3 g, 7.8 mmol) in diethyl ether (250 mL) containing CuOTf (0.2 g) under an Ar atmosphere was irradiated with a 450 W medium pressure mercury vapor lamp (Hanovia) through a double-walled water-cooled quartz immersion well for 6−7 h. The reaction mixture was then washed successively with ice-cold aqueous NH_4OH (2 × 20 mL) and water (2 × 20 mL) and dried. Removal of solvent followed by column chromatography [ether−petroleum (1:9)] of the residual oil afforded the cyclobutane derivative **6a** (0.65 g, 50%) as a colorless liquid: ^{1}H NMR (200 MHz) δ 1.13 (3H, s), 1.18 (3H, s), 1.57−1.83 (4H, m), 2.5 (1H, q, J = 6 Hz), 2.85 (1H, q, J = 6 Hz), 3.66 (1H, d, J = 10 Hz), 3.84−4.03 (2H, m), and 4.20 (1H, J = 7.5 Hz); ^{13}C NMR δ 20.1 (Me), 20.6 (Me), 25.9 (CH_2), 31.7 (CH_2), 36.4 (CH), 40.4 (CH), 68.3 (CH_2), 70.5 (CH_2), 78.4 (C_1 or C_2) and 96.45 (C_2 or C_1). Anal. Calcd. for $C_{10}H_{16}O_2$: C, 71.39 H, 9.58. Found: C, 70.92 H, 9.56.

Rearrangement of the Cyclobutane Derivative 6a. Synthesis of 2,2-Dimethyl-3-(hydroxymethyl)-5-(β-hydroxyethyl)cyclopentanone (10a). A solution of the cyclobutane derivative **6a** (0.25 g, 1.49 mmol) in TFA (1 mL) and TfOH (50 μL) was heated in an oil bath (50−55 °C) for 1 h. The reaction mixture was cooled, made alkaline by dropwise addition of aqueous NaOH (10%), and extracted with dichloromethane (3 × 10 mL). The organic extract was dried and concentrated. The residue was dissolved in MeOH (1 mL), and to it was added aqueous NaOH (1 mL, 20%). The mixture was refluxed for 45 min and on cooling to rt was extracted with ethyl acetate (2 × 15 mL). The organic extract was washed with brine, dried, and concentrated. The residual mass was chromatographed (ethyl acetate) to afford the cyclopentanone **10a** (0.155 g, 55%) as a yellow viscous liquid as an inseprable mixture in ca. 3:1 ratio (^{1}H and ^{13}C NMR) of the diastereoisomers epimeric at C_5; IR 3407, 1739 cm^{-1}; ^{1}H NMR (200 MHz) δ 0.84 and 1.10 (two s, Me's for the major diastereoisomer), δ 0.95 and 1.04 (two s, Me's for the minor), 1.58 (1H, m), 1.83−2.06 (3H, m), 2.27−2.56 (2H, m), 3.0 (br s), 3.53−3.79 (4H, m); ^{13}C NMR (for the major) δ 18.2 (Me), 24.5 (Me), 30 (CH_2), 33.3 (CH_2), 46.3 (CH), 47.6 (CH), 61 (CH_2), 63 (CH_2), 47.2 and 225.5; (for the minor ketone), δ 18.6, 24.9, 29, 34.6, 43.3, 46.7, 60.8, 63 and 226; EIMS m/z 186 (M^+) 169, 142 (100), 127, 109, 86, 55. Anal. Calcd for $C_{10}H_{18}O_3$: C, 64.48 H, 9.70. Found: C, 64.10 H, 9.71.

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Supporting Information Available: ^{1}H NMR spectra of **5**, **6**, **8**, **9**, **10a**,**b**,**d**,**e**, **12**, **14**, **15**, and **16**, ^{13}C NMR spectra of **6**, **9**, **10a**,**b**,**d**,**e**, **12**, and **15**, and mass spectra of **10a** and **12a** (54 pages). This material is contained in libraries on microfiche, immediately follows the article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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