2-methyl-5-isopropenyl-2-cyclohexen-1-ol, 99-48-9; 2-methyl-5-isopropenylcyclohexanol, 619-01-2; cyclopentanol, 96-41-3; 3-methylcyclopentanol, 18729-48-1; *N*-(1-cyclohexenyl)piperidine, 2981-10-4; *N*-(1-cyclohexenyl)morpholine, 670-80-4; *N*-(1-cyclohexenyl)pyrrolidine, 1125-99-1; *N*-(1-cyclopentenyl)morpholine, 936-52-7; ethyl 3-morpholino-2-butenoate, 36277-32-4; *N*-(cyclohexyl)piperidine, 3319-01-5; *N*-(cyclohexyl)morpholine, 6425-41-8; *N*-(cyclohexyl)pyrrolidine, 7731-02-4; *N*-(cyclopentyl)morpholine, 39198-78-2; ethyl 3-morpholinobutanoate, 42980-69-8; piperidine, 110-89-4; morpholine, 110-91-8; *N*-benzylpiperidine, 2905-56-8; *N*-benzylmorpholine, 10316-00-4; *N*-nonylpiperidine, 30538-80-8; *N*-methylcyclohexylamine, 100-60-7; *N*-cyclohexylallylamine, 6628-00-8; *N*-cyclohexylaniline, 1821-36-9; *N,N*-diethylcyclohexylamine, 91-65-6; dicyclohexylamine, 101-83-7; *N*-methyldicyclohexylamine·hydrochloride, 59325-20-1; 2-undecanone tosylhydrazone, 37826-47-4; 4-*tert*-butylcyclohexanone tosylhydrazone, 41780-53-4; cholestan-3-one tosylhydrazone, 37826-48-5; *tert*-butylcyclohexane, 3178-22-1; cholestane, 14982-53-7.

Diels–Alder Approach to Bicyclic α-Hydroxy Ketones. Facile Ketol Rearrangements of Strained α-Hydroxy Ketones

Xavier Creary,* Pamela A. Inocencio, Ted L. Underiner, and Ray Kostromin

Department of Chemistry, University of Notre Dame, Notre Dame, Indiana 46556

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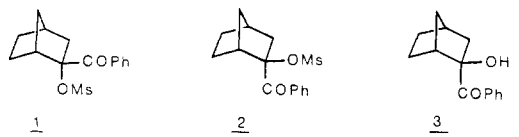
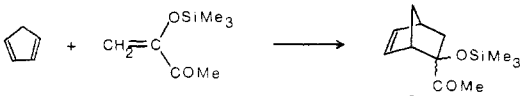
The trimethylsiloxy-substituted dienophiles 1-benzoyl-1-(trimethylsiloxy)ethylene, **6**, 1-carbomethoxy-1-(trimethylsiloxy)ethylene, **12**, and 1-acetyl-1-(trimethylsiloxy)ethylene, **4**, all reacted with cyclopentadiene to give adducts in which the carbonyl containing substituent of the major product occupied the exo position, in violation of the Alder rule. Desilylation of the Diels–Alder adducts of cyclopentadiene with **4** and **6** led to ring-expanded ketol rearrangement products on silica gel chromatography. This facile rearrangement was attributed to relief of strain in the starting α-hydroxy ketone. Equilibration studies showed that in the rearranged 2-hydroxy-2-substituted bicyclo[3.2.1]octan-3-one systems **24** and **30**, the more stable isomer is the one in which the phenyl or methyl substituent is in the axial position. The presence of a strong intramolecular hydrogen bond of the equatorial hydroxyl group with the carbonyl group accounts for the greater stability of **24** and **30**. Acetolysis of *endo*-2-benzoyl-*exo*-2-norbornyl mesylate, **2**, occurred readily, giving mainly the rearranged product of internal return, 1-benzoyl-*exo*-2-norbornyl mesylate, **38**. The high reactivity of **2** relative to the endo analogue and the α-H analogue was attributed to some transition-state carbonyl conjugation with the incipient α-keto cation center as well as possible neighboring σ-participation and/or steric rate enhancement.

During the course of studies[1] designed to generate and evaluate the properties of α-keto cations, we have prepared the *endo* mesylate **1**.[1c] We wanted to prepare the *exo* mesylate **2** in order to compare the behavior of these two



1 **2** **3**

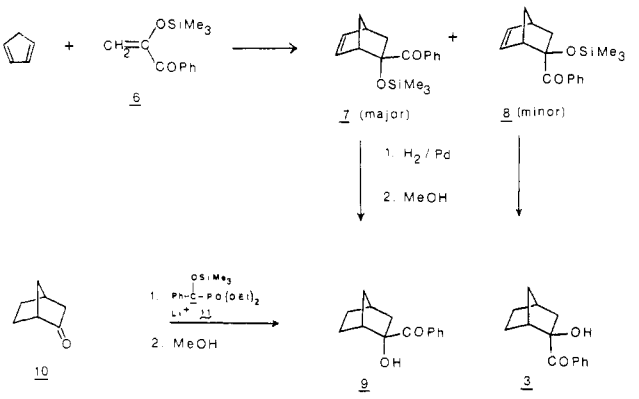
systems. Hence we desired a synthetic route to the precursor exo alcohol **3**. It has been reported[2] that cyclopentadiene reacts with **4** to give an adduct which, when desilylated, gives an α-hydroxy ketone presumed (but not proven) to have the hydroxy group in the exo position. Reported here are our attempts to prepare **3** using a similar Diels–Alder approach.



4 **5**

Results and Discussion

Diels–Alder Reactions of Trimethylsiloxy-Substituted Dienophiles. Our approach to the synthesis of **3** involved in Diels–Alder reaction of cyclopentadiene with the enone **6**. This reaction gave a 58% yield of a mixture



of **7** (3.5 parts) and **8** (1 part) in which, unexpectedly, the isomer **7**, with the endo trimethylsiloxy group, predominated. The stereochemical assignment was confirmed by catalytic hydrogenation of the mixture followed by desilylation. The major ketol **9** was identical with a sample produced independently by addition of the benzoyl anion equivalent **11** to norcamphor.[1c]

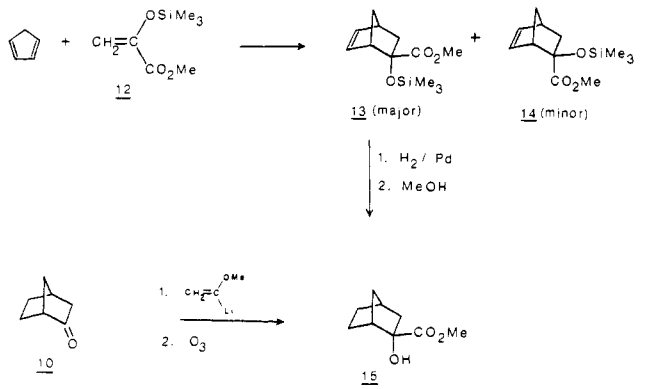
In view of the surprising stereochemistry of this Diels–Alder reaction, the reaction of other dienophiles, which are structurally similar to **6**, was examined. Reaction of **12** with cyclopentadiene gave two adducts in which, as before, the endo trimethylsiloxy adduct **13** predominates. The stereochemistry was likewise established by hydrogenation and desilylation of **13**, which gave a product indentical with **15** produced by addition of (α-methoxyvinyl)lithium to norcamphor followed by ozonolysis.[1c]

In view of these results, the previously reported[2] reaction of **4** with cyclopentadiene was repeated. The Diels–Alder adducts **16** and **17** were isolated in 48% overall yield prior

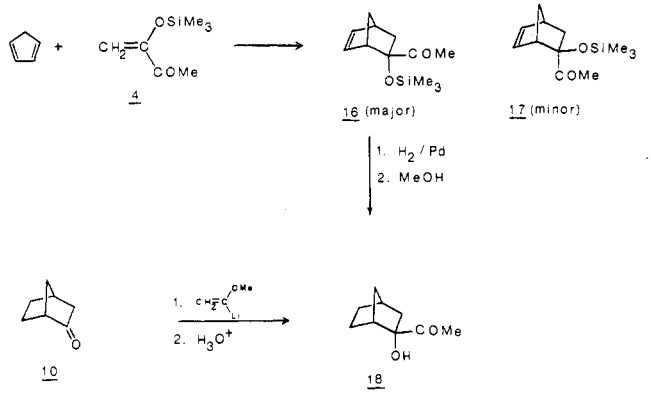
(1) (a) Creary, X. *J. Org. Chem.* **1979**, *44*, 3938–45. (b) Creary, X. *J. Am. Chem. Soc.* **1981**, *103*, 2463–5. (c) Creary, X.; Geiger, C. C. *Ibid.* **1982**, *104*, 4151–62. (d) Creary, X.; Geiger, C. C. *Ibid.* **1983**, *105*, 7123–9. (e) Creary, X. *Ibid.* **1984**, *106*, 5568–77.

(2) Ardecky, R. J.; Kerdesky, F. A. J.; Cava, M. P. *J. Org. Chem.* **1981**, *46*, 1483–5.

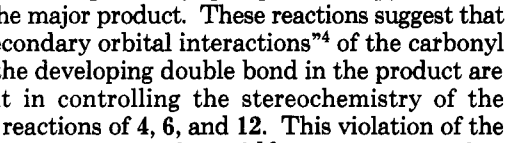
0022-3263/85/1950-1932$01.50/0



to desilylation. As before, independent synthesis established that the major adduct **16** had the trimethylsiloxy group in the endo configuration.

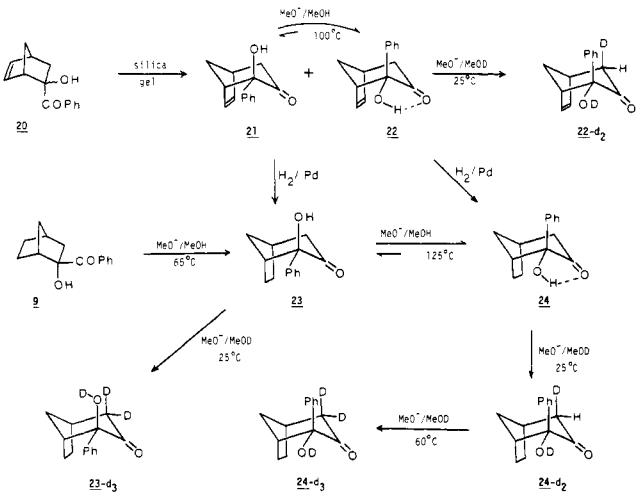


This preferred endo orientation of the trimethylsiloxy group in all of these Diels–Alder reactions is unexpected on the basis of the Alder rule[3] which predicts that the electron-withdrawing carbonyl group will occupy the endo position of the major product. These reactions suggest that so called "secondary orbital interactions"[4] of the carbonyl group with the developing double bond in the product are unimportant in controlling the stereochemistry of the Diels–Alder reactions of **4**, **6**, and **12**. This violation of the Alder rule is not unprecedented.[5,6] Previous studies showed that the methacrylic dienophiles **19** gave preferential exo orientation of the electron-withdrawing substituent Y in Diels–Alder reactions with cyclopentadiene[5] and homo Diels–Alder reactions with norbornadiene.[5b] These stereochemical results have been interpreted in terms of a stabilizing Van der Waals interaction between the methyl group of the dienophile and the unsaturated center of the diene.[5b] Other pertinent examples, where violation of the Alder rule occur, have also appeared.[6] Mark[6a] has pointed out that "when not in competition with hydrogen, unsaturated substituents tend to violate the rule of endo addition..." Our current study, using the trimethylsiloxy group, should serve to emphasize this little appreciated point.[7]



19

Desilylation of α-Trimethylsiloxy Ketones. Attention was next turned to desilylation of the unsaturated adducts **7** and **8**. Treatment with 10^{-3} M trifluoroacetic acid in methanol followed by silica gel chromatography gave two α-hydroxy ketones which contained no benzoyl group as evidenced by infrared and NMR spectroscopy. The ratio of these two products was not reproducible but appeared to depend on the history of the silica gel and the polarity of the solvent used in the chromatography. Apparently a ketol rearrangement[8] of the initially formed products **20** occurred on silica gel chromatography. Of the four potential rearrangement products, the two ketol products formed were assigned as structures **21** and **22** based on the following data. Treatment of the chromatographed mixture of **21** and **22** with 0.5 M sodium methoxide in methanol at 100 °C resulted in an equilibrated mixture in which **22** predominated (89:11 mixture). Catalytic hydrogenation of **21** gave a saturated ketol **23**, which could be produced independently on treatment of **9** with methoxide at 64 °C. Catalytic hydrogenation of **22** gave a second saturated ketol, **24**, which could also be prepared independently when **23** was heated with 0.5 M methoxide at 125 °C. The 2-keto regioisomers **25** and **26** were ruled out as products by a series of deuterium exchange experiments. Ketol **22** readily exchanged a single hydrogen α to the carbonyl group on treatment with 0.1 M methoxide in CH_3OD. The saturated analogue **24** also



(3) (a) Alder, K.; Stein, G. *Angew. Chem.* **1937** *50*, 514. (b) Alder, K. *J. Liebigs Ann. Chem.* **1951**, *571*, 157–64. See also: (c) Martin, J. G.; Hill, R. K. *Chem. Rev.* **1961**, *61*, 537–62.

(4) Woodward, R. B.; Hoffman, R. In "The Conservation of Orbital Symmetry"; Verlag Chemie: Weinheim/Bergstr, Germany, and Academic Press: New York, 1970; p 145.

(5) (a) Kobuke, Y.; Fueno, T.; Furukawa, J. *J. Am. Chem. Soc.* **1970**, *92*, 6548–53, (b) Kobuke, Y.; Sugimoto, T.; Furukawa, J.; Fueno, T. *Ibid.* **1972**, *94*, 3633–5. (c) Berson, J. A.; Hamlet, J.; Mueller, W. A. *Ibid.* **1962**, *84*, 297–304. (d) Alder, K.; Günzl, W. *Chem. Ber.* **1960**, *93*, 809–825. (e) Schwarz, M.; Marienthal, M. *J. Org. Chem.* **1960**, *25*, 449–52. (f) Boehme, W. R.; Schipper, E.; Scharpf, W. G.; Nichols, J. *J. Am. Chem. Soc.* **1958**, *80*, 5488–95. (g) Alder, K.; Hartmann, R.; Roth, W. *Justus Liebigs Ann. Chem.* **1958**, *613*, 6–27.

(6) (a) Mark , V. *J. Org. Chem.* **1974**, *39*, 3181–3. (b) McBee, E. T.; Keogh, M. J.; Levek, R. B.; Wesseler, E. P. *Ibid.* **1973**, *38*, 632–6. (c) Mellor, J. M.; Webb, C. F. *J. Chem. Soc., Perkin Trans. 2* **1974**, 17–22, 26–31. (d) Cantello, B. C. C.; Mellor, J. M.; Webb, C. F. *Ibid.* **1974**, *22*–5.

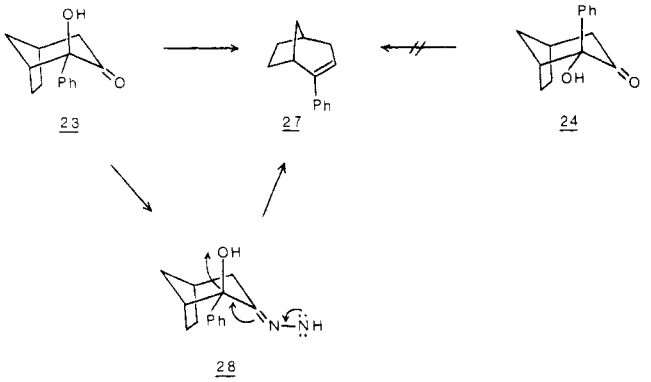
(7) Reaction of the methoxy and acetoxy dienophiles i and ii with cyclopentadiene also gave the benzoyl group in the exo position of the major product. Exo/endo benzoyl ratios were 1.26 and 1.32, respectively.

(8) This reaction can be either acid or base catalyzed. For a discussion of this general rearrangement, see: (a) Nickon, A.; Nishida, T.; Lin, Y. *J. Am. Chem. Soc.* **1969**, *91*, 6860–1. (b) Eastham, J. F.; Huffaker, J. E.; Raaen, V. F.; Collins, C. J. *Ibid.* **1956**, *78*, 4323–8. (c) Curtin, D. Y.; Leskowitz, S. *Ibid.* **1951**, *73*, 2633–6. (d) Mazur, Y.; Nussim, M. *Tetrahedron Lett.* **1961**, *817*–21. (e) Elphimoff-Felkin, I.; Genevieve; L. N.; Tchoubar, B. *Bull. Soc. Chim. Fr.* **1958**, 522–31.

25 26

exchanged a single α-keto hydrogen at room temperature and both protons at 60 °C in CH_3OD. The saturated ketol **23** readily exchanged both α-keto hydrogens at room in CH_3OD.

The stereochemistries of these ketols were established by a combination of infrared spectral analyses and chemical reactivities. Under Wolfe–Kishner conditions (Huang–Milon modification), **23** gave only the product of reductive elimination, the alkene **27**.[1c] Under similar conditions, no **27** is produced from **24**. This suggests that the hydroxyl group is axial in **23**[9] and elimination of this axial group is facile under Wolfe–Kishner conditions.

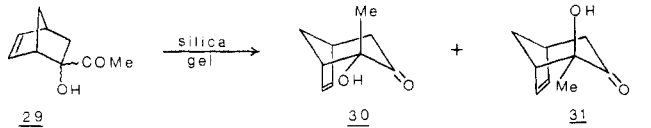


23 27 24

28

Infrared spectral data also support the suggested stereochemistries of **23** and **24**. In carbon tetrachloride, the less stable isomer **23** shows both a sharp, free O–H stretch at 3620 cm^{-1} and a broad, intermolecular hydrogen-bonded O–H stretch at 3470 cm^{-1}. In contrast, the more stable isomer **24** showed only an intramolecularly hydrogen-bonded O–H stretch at 3550 cm^{-1} No free OH stretch was observed even in dilute solutions. Molecular models show that intramolecular hydrogen bonding is much more favorable with an equatorial hydroxyl group. Apparently the strength of the intramolecular hydrogen bond in the equatorial alcohol **24** more than offsets the effect of placing the phenyl group in the axial environment. Isomers **24** and **22** therefore predominate at equilibrium in these ketol rearrangement manifolds.

Desilylation of **16** and **17** gave the ketols **29**, which underwent analogous ketol rearrangements under silica gel chromatography conditions.[10] As before the extent of the



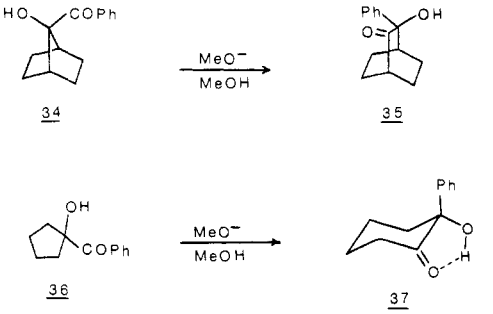
29 30 31

rearrangement was dependent on the chromatography conditions. These products were also formed in attempts to separate the mixture **29** by preparative gas chromatography. The bottom of this ketol rearrangement manifold is the ketol **30** (which readily exchanges the α-keto hydrogen in CH_3OD/methoxide solution and shows only an intramolecular hydrogen bonded O–H stretch in the infrared).

We have observed that the ketol rearrangements observed are a delicate function of strain in the system. The strained cyclobutyl system **32** rearranges completely to **33** on silica gel chromatography. While the unsaturated

32 33

ketols **20** (and **29**) rearrange, the saturated analogues **3** and **9** survive silica gel chromatography unscathed. Ketols **34** and **36** also survive chromatography and refluxing sodium



34 35

36 37

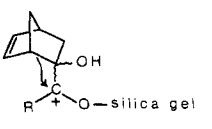
methoxide in methanol is necessary to induce rearrangements of these ketols. The additional ring strain, as a result of the double bonds in the unsaturated systems **20** and **29**, is apparently enough to make ketol rearrangements a facile process in these systems. Catalysis is probably a result of acidic sites on the silica gel surface.[11]

Solvolytic Studies on Mesylate 2. Having successfully prepared the α-hydroxy ketone **3** (albeit in low yield), separation from the isomer **9** was achieved by silica gel chromatography. Conversion to the mesylate **2** was accomplished by peracid oxidation of the sulfinate ester derived from **3**. Solvolysis of **2** in acetic acid at 25 °C was complicated by a large amount of internal return giving the rearranged β-keto mesylate **38** as the major product, along with the rearranged acetate **39**. At higher temperatures **38** also solvolyzed giving **39**, as well as the elimination products **40** and **41**. Interestingly, the α-keto mesylate **2** is much more reactive than the β-keto mesylate **38**, despite the fact that the electron-withdrawing carbonyl group is one carbon further removed from the incipient carbocationic center in **38**. This same phenomenon has been observed by Gassman et al.[12] who found that α-cyano tosylates were more reactive than β-cyano analogues. This unexpected high reactivity in the α-cyano systems was attributed to a conjugative effect which partially offset the

(9) Electron diffraction studies show that the unsubstituted hydrocarbon bicyclo[3.2.1]octane exists preferentially in the chair conformation. See: Mastryukov, V. S.; Osina, E. L.; Vilvok, L. V.; Hilderbrandt, R. L. *Zh. Strukt. Khim.* **1981**, *22*, 57. Force field calculations indicate that the boat form of this hydrocarbon is 6.45 kcal/mol higher in energy than the chair form. See: Maier, W. F.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 1891–1900.

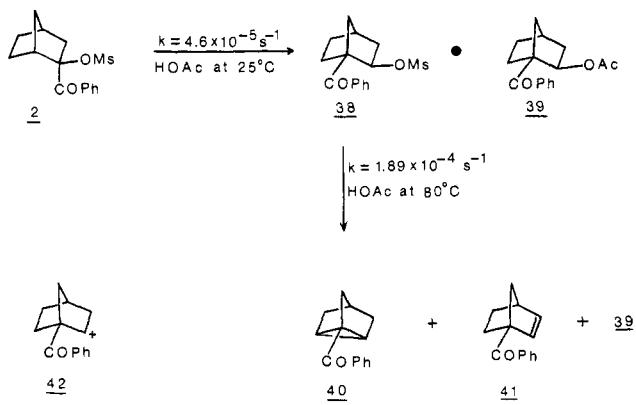
(10) The previously reported data[2] for the product of desilylation of **29** is consistent with a ketol rearranged product and not a bicyclo[2.2.1]heptane system. Professor Cava (private communication) is in accord with this assessment.

(11) We envisage rearrangement occurring via migration of the allylic carbon to the electron-deficient carbon of a coordinated carbonyl group as in iii. The ease of rearrangement of **20** and **29** may also be reflecting the greater migratory apptitude of the allyl center in iii relative to the saturated center in the saturated analoues.



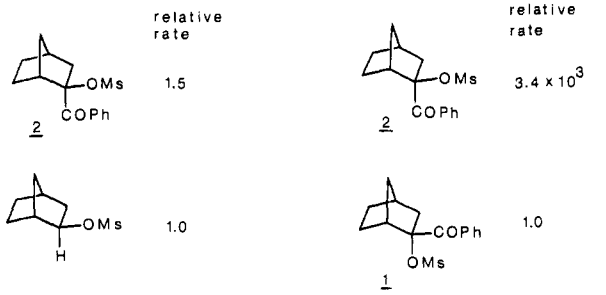
iii

(12) For a review and leading references, see: Gassman, P. G.; Tidwell, T. T. *Acc. Chem. Res.* **1983**, *16*, 279–85.



inductive effect of the electronegative cyano group.

The α-keto mesylate **2** is also 1.5 times more reactive than the α-H analogue *exo*-2-norbornyl mesylate[13] and 3.4 × 10^3 times more reactive than the endo analogue **1**.[1c]



Three factors may contribute to the high reactivity of **2**. First, a rate-retarding inductive effect of the carbonyl group is not apparent in solvolysis of **2**. This may be attributed to carbonyl conjugation in the transition state for solvolysis of **2** which negates the inductive effect of this group. A second factor could be anchimeric assitance due to σ-participation[14] in **2** which results in a slightly larger exo/endo ratio (3400)[15] than seen in the parent 2-norbornyl system (1600).[16] Such participation would lead to the β-keto cation **42** as the first intermediate, bypassing a discrete α-keto cation. A third factor could be a steric rate enhancement due to relief of an unfavorable interaction of the endo benzoyl group of **2** with the endo 6-hydrogen. This may contribute a small factor to the high reactivity of **2** but cannot completely account for the fact that this electronegatively substituted substrate is even *more* reactive than the α-H analogue. It is not possible to assess the relative contributions of these three factors to the reactivity of **2** with the available data. However, we feel that some transition-state carbonyl conjugation is also necessary to account for the reactivity of **2** relative to the α-H analogue.

Conclusions. Diels–Alder reactions of cyclopentadiene with the siloxy-substituted dienophiles **4**, **6**, and **12** all gave major adducts in which the carbonyl group occupied the exo position. The Alder rule is apparently not valid in predicting stereochemistries of these Diels–Alder reactions. The α-hydroxy ketone products formed on desilylation of these unsaturated bicyclic α-trimethysiloxy ketones all rearranged rapidly on silica gel chromatography, giving ring expanded ketols. This facile rearrangement on silica gel, which also occurs for the cyclobutyl system **32**, was attributed to relief of strain in the parent ketols. Intramolecular hydrogen bonding in **22**, **24**, and **30** resulted in greater stability of these ketols containing the equatorial hydroxyl group.

Finally, solvolysis of mesylate **2** was quite facile, giving products of Wagner–Meerwein rearrangement and internal return or solvent capture. The high reactivity of **2** was attributed to transition-state carbonyl conjugation with the developing cationic center and possibly neighboring σ-participation leading to a β-keto cation. Another potential rate enhancing feature was relief of an unfavorable endo benzoyl steric interaction. The available data do not allow one to decide on the discrete intermediacy of an α-keto cation.

Experimental Section

Gas chromatographic analyses were carried out on a Hewlett-Packard 5750 chromatograph with flame ionization detector using a 6 ft 5% SE-30 on Chromosorb G column. A Varian 920 chromatograph was used for sample isolation. NMR spectra were recorded on a Varian EM 390 or a Nicolet NB 300 spectrometer. Infrared spectra were recorded on a Perkin-Elmer 727B spectrometer. Titrations were carried out on a Metrohm E576 automatic recording titrator.

Preparation of 1-Benzoyl-1-(trimethylsiloxy)ethylene, 6. A solution of 10.87 g of 1-phenylpropane-1,2-dione[17] and 10.68 g of chlorotrimethylsilane in 70 mL of ether was stirred at room temperature as 10.6 g of triethylamine was added dropwise. After being stirred for 5 h at room temperature, the mixture was diluted with 100 mL of Skelly F and the triethylamine hydrochloride was removed by filtration through a Büchner funnel. The filtrate was washed with cold water and saturated NaCl solution and dried over $MgSO_4$. the solvent was removed by rotary evaporator, and the residue was distilled through a short path condenser. A 1.68-g forerun containing unreacted 1-phenylpropane-1,2-dione and about 50% of **6** was collected at 0.2 mm. The main fraction of **6** was next collected giving 10.18 g (63%): bp 57–60 °C (0.04 mm); NMR ($CDCl_3$) δ 7.90–7.7 (2 H, m), 7.7–7.3 (3 H, m), 5.18 (2 H, m), 0.23 (9 H, s). This material degraded on standing at room temperature for extended periods.

Reaction of Cyclopentadiene with 6. A mixture of 10.04 g of **6** and 14.6 g of cyclopentadiene was heated in a tightly stoppered flask at 65 °C for 90 min and at 70 °C for 150 min. The dicyclopentadiene was removed by distillation through an 18-cm Vigreux column at 5 mm. The Vigreux column was then removed, and the mixture was distilled by using a short-path distillation head. A 9.68-g fraction boiling at 70–87 °C (0.06 mm) was collected and consisted of unreacted **6** and a mixture of **7** and **8**. This fraction was redistilled through an 18-cm Vigreux column. A fraction boiling at 55–70 °C (0.05 mm) was collected and consisted of mostly **6**. The Vigreux column was removed and 7.53 g (58%) of a mixture of **7** and **8** was collected: bp 90–100 °C (0.05 mm). The olefinic protons of **7** appear at δ 6.44 and 6.19 (doublet of doublets, J = 5.4, 3.2 Hz). The olefinic protons of **8** appear at δ 6.12 and 5.90 (doublet of doublets, J = 5.4, 3.2 Hz). the trimethylsiloxy protons appear at δ −0.12 for **7** and 0.01 for **8**. The ration of **7** to **8** was 3.5:1 as determined by 300-MHz NMR.

Hydrogenation of 7 and 8. A 3.30-g sample of the mixture of **7** and **8** (from the reaction of cyclopentadiene with **6**) was dissolved in 30 mL of ether and 100 mg of 10% palladium on charcoal was added. The mixture was hydrogenated (Parr Hydrogenator) at 55 psi for 75 min and filtered through Celite, and

(13) k_{HOAc} = 3.17 × 10^{-5} s^{-1} at 25 °C. This rate is 1.36 times faster than the corresponding tosylate. See: Schleyer, P. v. R.; Donaldson, M. M.; Watts, W. E. *J. Am. Chem. Soc.* **1965**, *87*, 375–6. (b) Winstein, S.; Trifan, D. *Ibid.* **1952**, *74*, 1147–54, 1154–60. The rate ratio of **2** to *exo*-2-norbornyl mesylate of 3.3 is probably not a good measure of actual ionization rate ratios, since *exo*-2-norbornyl mesylate is probably subject to a large amount of internal return.

(14) For a detailed discussion of this controversial area, see: (a) Brown, H. C. "The Nonclassical Ion Problem"; Plenum Press: New York, 1977. (b) Grob, C. A. *Acc. Chem. Res.* **1983**, *16*, 426–31. (c) Brown, H. C. *Ibid.* **1983**, *16*, 432–40. (d) Olah, G. A.; Prakash, G. K. S.; Saunders, M. *Ibid.* **1983**, *16*, 440–8. (e) Walling, C. *Ibid.* **1983**, *16*, 448–54.

(15) For an example of a greatly increased exo/endo rate ratio due to σ-participation in a secondary α-keto system, see ref 1d.

(16) This value is based on racemization rates of 2-norbornyl brosylates. See ref 13b and Winstein, S.; Clippinger, E.; Howe, R.; Vogelfanger, E. *J. Am. Chem. Soc.* **1965**, *87*, 376–7.

(17) Emmons, W. D.; Freeman, J. P. *J. Am. Chem. Soc.* **1955**, *77*, 4415–6.

the solvent was removed by rotary evaporator. The residue (3.25 g) was dissolved in 25 mL of 10^{-3} M trifluoroacetic acid in methanol. After 20 h at room temperature, gas chromatography analysis showed no remaining **7** and **8**. The methanol was removed by rotary evaporator leaving a quantitative yield of **9** and **3**. Gas chromatographic analysis (5% SE 30 on Chromosorb G column) showed that the major product had the same retention time as an authentic sample[1c] of **9**. The entire product mixture was chromatographed in 60 g of silica gel and eluted with increasing amounts of ether (up to 20%) in Skelly F. The major product **9** eluted first and was identified by spectral comparison with an authentic sample. Mixtures of **9** and **3** next eluted, followed by pure **3**: mp 71–72 °C; NMR ($CDCl_3$) δ 8.2–8.1 (2 H, m), 7.57–7.39 (3 H, m), 2.68 (1 H, m), 2.58 (1 H, doublet of doublets), 2.37 (1 H, m) 2.07–1.99 (2 H, m), 1.6–1.3 (4 H, m), 1.28–1.17 (1 H, m), 1.06–0.95 (1 H, m). Anal. Calcd for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46. Found: C, 77.60; H, 7.50.

Desilylation of 7 and 8. A solution of 310 mg of the mixture of **7** and **8** (from the reaction of cyclopentadiene with **6**) in 25 mL of 10^{-3} M trifluoroacetic acid was kept at room temperature for 34 min. No starting material remained by gas chromatographic analysis. About 5 mg of Et_3N was added, and the methanol was removed by rotary evaporator leaving a quantitative yield of a mixture of ketols. The 300-MHz NMR spectrum showed both isomers of the unrearranged ketols **20** in a 3.5:1 ratio. The olefinic hydrogens of **20** (exo benzoyl, endo hydroxyl) appear at δ 6.618 (doublet of doublets) and 6.264 (doublet of doublets). The olefinic hydrogens of **20** (exo hydroxyl, endo benzoyl) appear at δ 6.115 (doublet of doublets) and 5.971 (doublet of doublets). In a separate desilylation, small amounts of the rearranged ketols **21** and **22** were observed.

The above mixture of ketols **20** was chromatographed on 5 g of silica gel in a column packed with 5% ether in Skelly F. The column was eluted with increasing percentages of ether. The product eluted with about 20% ether in Skelly F. Solvent was removed from the combined fractions, and the residue was analyzed by 300-MHz NMR which showed complete disappearance of the signals at δ 6.618 and 6.264 due to **20** (exo benzoyl, endo hydroxyl). The signals at δ 6.115 and 5.971 due to **20** (exo hydroxyl, endo benzoyl) were now present in only small amounts (2%). Ketols **21** and **22** were the major components of the mixture in a 3.7:1 ratio. In a separate silica gel chromatography, the ratio of **21** to **22** was 0.46:1. The olefinic hydrogens of **21** appear at δ 6.220 and 5.479. The olefinic hydrogens of **22** appear as an AA'BB' pattern centered at δ 6.197.

In a separate chromatography on silica gel, a sample of ketol **20** (exo benzoyl, endo hydroxyl), prepared by addition of lithium diethyl-1-(trimethylsiloxy)-1-phenylmethanephosphonate[18] to bicyclo[2.2.1]hept-5-en-2-one, was chromatographed and gave complete rearrangement to **22**: NMR ($CDCl_3$) δ 7.22–7.10 (5 H, m), 6.217 (1 H, olefin, doublet of doublets of doublets, J = 5.7, 2.7, 0.6 Hz), 6.176 (1 H, olefin, doublet of doublets of doublets, J = 5.7, 2.7, 0.6 Hz), 3.962 (1 H, s), 3.49 (1 H, m), 2.92 (1 H, m), 2.75–2.55 (2 H, m), 2.05 (1 H, m), 1.86 (1 H, d, J = 12 Hz).

Preparation of 1-Carbomethoxy-1-(trimethylsiloxy)-ethylene, 12. A solution of 2.97 g of methyl pyruvate and 3.73 g of chlorotrimethylsilane in 20 mL of ether was stirred at room temperature as 4.18 g of triethylamine was added dropwise. After 3.5 h at room temperature, the mixture was diluted with about 45 mL of Skelly F and filtered. The filtrate was washed with cold water and saturated NaCl solution and dried over $MgSO_4$. The solvent was removed by rotary evaporator, and the residue was distilled. After a small forrun, the product distilled giving 3.09 g (61%) of **12**: bp 61–64 °C (15 mm); NMR ($CDCl_3$) δ 5.49 (1 H, d, J = 1.2 Hz), 4.88 (1 H, d, J = 1.2 Hz), 3.75 (3 H, s), 0.22 (9 H, s). Alkene **12** gave a white insoluble polymer on standing at room temperature.

Reaction of Cyclopentadiene with 12. A mixture of 1.5 g of **12** and 2.7 g of cyclopentadiene was heated in a sealed tube at 70 °C for 5 h 45 min. Gas chromatographic analysis showed a large amount of dicyclopentadiene, much unreacted **12**, and a low yield of an inseparable mixture of adducts **13** and **14**. The unreacted **12** and much of the dicyclopentadiene were removed by distillation using a short-path distillation head at 20 mm. A mixture of dicyclopentadiene and esters **13** and **14** was collected at 1.8 mm. The 300-MHz NMR of this mixture showed **13** and **14** in a 2.4:1 ratio. A sample of these esters isolated by preparative gas chromatography had the same product ratio. The olefinic hydrogens of **13** appear at δ 6.34 (doublet of doublets) and 6.08 (doublet of doublets). The methoxy group appears at δ 3.764 and the trimethylsiloxy group at δ 0.059. The olefinic hydrogens of **14** appear at δ 6.23 (doublet of doublets) and 5.87 (doublet of doublets). The methoxy group appears at δ 3.674 and the trimethylsiloxy group at δ 0.116.

Hydrogenation of 13 and 14. A solution of 66 mg of a mixture of **13** and **14** in 10 mL of ether containing 100 mg of 10% Pd on charcoal was hydrogenated at 40 psi for 3 h. After being filtered through Celite, and solvent was removed by rotary evaporator and 4 mL of 10^{-3} M trifluoroacetic acid in methanol was added. After 12 h, the solvent was removed by rotary evaporator. The gas chromatographic retention time (5 ft 15% Carbowax 20 M on Chromosorb P column) of the major product was identical with that of an authentic sample[1c] of **15**. The 300-MHz NMR spectrum showed **15** (methoxy group at δ 3.784) and the isomeric *exo*-2-hydroxy-*endo*-2-carbomethoxybicyclo[2.2.1]heptane (methoxy group at δ 3.772) in a 2.4:1 ratio.

Reaction of 1-Acetyl-1-(trimethylsiloxy)ethylene, 4, with Cyclopentadiene. A mixture of 1.22 g of **4**[19] and 1.40 g of cyclopentadiene (unreacted after 1 h at room temperature) was heated in a sealed tube at 70 °C for 6.5 h. The mixture was distilled through an 18-cm Vigreux column. After a forerun containing unreacted **4** and dicyclopentadiene, 0.82 g (48%) of a mixture of **16** and **17** was collected; bp 82–85 °C (2.7 mm). **16**: NMR ($CDCl_3$) δ 6.37 (doublet of doublets, olefinic H), 6.42 (doublet of doublets, olefinic H), 2.308 (s, CH_3), 0.044 (s, $OSiMe_3$). **17**: NMR ($CDCl_3$) δ 6.18 (doublet of doublets, olefinic H), 5.81 (doublet of doublets, olefinic H), 2.192 (s, CH_3), 0.120 (s, $OSiMe_3$). The remaining hydrogens of **16** and **17** appear between δ 3.0 and 1.0. The ratio of **16** andd **17** was 2.57:1 as determined by 300-MHz NMR.

Hydrogenation of 16 and 17. A 420-mg sample of the mixture of **16** and **17** (from the reaction of cyclopentadiene with **4**) was dissolved in 15 mL of ether, and 60 mg of 10% palladium on carbon was added. The mixture was hydrogenated at 55 psi for 1.5 h. After being filtered through Celite, the solvent was removed by rotary evaporator and the residue was dissolved in 5 mL of 10^{-3} M trifluoracetic acid in methanol. After 30 min, a drop of triethylamine was added and the solvent was removed by rotary evaporator. The residue was distilled by using a short-path distillation head to give 263 mg (92%) of a mixture of **18** and *endo*-2-acetyl-*exo*-bicyclo[2.2.1]heptan-2-ol, bp 90 °C (2 mm). The major isomer in this mixture was **18** which was identified by 300-MHz NMR spectral comparison with an authentic sample prepared as described below. The methyl group of **18** appears at δ 2.289 and the methyl group of *endo*-2-acetyl-*exo*-bicyclo-[2.2.1]heptan-2-ol appears at δ 2.268.

Preparation of *exo*-2-Acetyl-*endo*-bicyclo[2.2.1]heptan-2-ol, 18. To a solution of 530 mg of *exo*-2-(1-methoxyvinyl)-*endo*-bicyclo[2.2.1]heptan-2-ol[1c] in 5 mL of THF was added 3 mL of 2% sufluric acid in water. After 75 min at room temperature, a Na_2CO_3 solution was added and the mixture was taken up into ether. The organic phase was washed with water and saturated NaCl solution and dried over $MgSO_4$. The solvent was removed by rotary evaporator, and the residue was distilled giving 445 mg (92%) of **18**: bp 90–91 ° (1.8 mm); NMR (C DCl_3) δ 2.99 (1 H, b s), 2.36–1.99 (6 H, multiplet with sharp singlet at δ 2.289), 1.72–1.55 (2 H, m), 1.49–1.32 (4 H, m), 1.08 (1 H, doublet of doublets). Anal. Calcd for $C_9H_{14}O_2$: C, 78.21; H, 10.21. Found: C, 78.13; H, 10.15.

Desilylation of 16 and 17. A solution of 122 mg of a mixture of **16** and **17** in 2 mL of 10^{-3} M trifluoroacetic acid in methanol was kept at room temperature for 37 min. About 2 mg of triethylamine was added, and the solvent was removed by rotary

(18) (a) Koenigkramer, R. E.; Zimmer, H. *J. Org. Chem.* **1980**, *45*, 3994–8. (b) Koenigkramer, R. E.; Zimmer, H. *Tetrahedron Lett.* **1980**, *1017*–20.

(19) (a) Barnier, J. P.; Garnier, B.; Girard, C.; Denis, J. M.; Salaun, J.; Conia, J. M. *Tetrahedron Lett.* **1973**, 1747–50. (b) Murai, S.; Ryu, I.; Kandono, Y.; Katayama, H.; Kondo, K.; Sonada, N. Conia, *Lett.* **1977**, 1219–22.

evaporator. The NMR spectrum of the residue (81 mg, 100%) showed a mixture of ketols **29**. The major product (2.5 parts) (exo acetyl, endo hydroxyl), showed olefinic signals at δ 6.555 (doublet of doublets, J = 5.6, 3.5 Hz) and 6.200 (doublet of doublets, J = 5.6, 3.5 Hz), and a methyl singlet at δ 2.360. The minor product (1 part), (exo hydroxyl, endo acetyl), showed olefinic signals at δ 6.318 (doublet of doublets, J = 5.6, 3.5 Hz) and 6.011 (doublet of doublets, J = 5.6, 3.5 Hz) and a methyl singlet of δ 2.170.[20]

The above mixture was chromatography on 5 g of silica gel and eluted with increasing amounts of ether in Skelly F. The eluant was analyzed by 300-MHz NMR which showed the rearranged ketols **30** and **31** along with **29** (exo acetyl, endo hydroxyl) and **29** (exo hydroxyl, endo acetyl) in a 25:8.1:3.6:1.0 ratio, respectively. The ratio of products formed on chromatography of **29** on silica gel was not reproducible. On one occasion, silica gel chromatography of **29** gave only **30**. Attempted preparative gas chromatography (SE 30 column) of **29** also gave mixtures of rearranged and unrearranged products. A pure sample of **31** could be isolated by preparative gas chromatography. **30**: NMR ($CDCl_3$) δ 6.133 (1 H, doublet of doublets, J = 5.9, 2.6 Hz), 6.050 (1 H, doublet of doublets, J = 5.9, 2.6 Hz), 3.527 (1 H, s, exchanges with D_2O), 2.92 (1 H, m), 2.87 (1 H, m), 2.62 (1 H, doublet of doublets), 2.41 (1 H, doublet of triplets), 2.05 (2 H, m), 1.423 (3 H, s); IR (CCl_4) 3560 cm^{-1} (OH), 1710 cm^{-1} (C=O). **31**: NMR ($CDCl_3$) δ 6.189 (1 H, doublets, J = 5.7, 2.7 Hz), 5.943 (1 H, doublet of doublets, J = 5.7, 2.7 Hz), 2.84 (1 H, m), 2.77 (1 H, doublet of doublets), 2.70 (1 H, doublet of doublets, J = 17, 2.7 Hz), 2.27 (1 H, doublet of triplets, J = 17, 2 Hz), 2.29 (1 H, doublet, J = 10.5 Hz), 2.00 (1 H, s, exchanges with D_2O), 2.02–192 (1 H, m), 1.257 (3 H, s);[21] IR (CCl_4) 3630 (sharp), 3470 (br, OH), 1710 cm^{-1} (C=O).

Preparation of 23 from 9. The isomerization of **9** to **23** has previously been described.[1c] In the present reaction, reflux of 1.91 g of **9** in 19 mL of 0.5 M $NaOCH_3$ in methanol for 1 h gave, after a standard aqueous workup, 1.80 g of crude product. Recrystallization from 11 mL of cyclohexane gave 1.31 of pure **23**: mp 100–101 °C; IR (CCl_4) 3620 (sharp, free OH), 3480 (br, hydrogen bonded OH), 1715 cm^{-1} (C=O). This product was identical with the major product formed on catalytic hydrogenation of the mixture of **21** and **22** (from silica gel chromatography of **20**). **23**: 300-MHz NMR ($CDCl_3$) δ 7.4–7.2 (5 H, m), 2.903 (1 H, doublet of doublets of doublets, J = 17, 4.6, 2.1 Hz), 2.760 (1 H, s), 2.58–2.46 (2 H, m), 2.415 (1 H, br, doublet, J = 12 Hz), 2.337 (1 H, doublet of triplets, J = 17, 2.6 Hz), 1.89–1.72 (1 H, m), 1.70–1.38 (4 H, m). The signals at δ 2.903 and 2.337 are concentration dependent. Anal. Calcd for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46. Found: C, 77.68; H, 7.42.

Equilibration of 23 and 24. A solution of 72.6 mg of **23** in 1 mL of 0.5 M sodium methoxide in methanol was sealed in two tubes. The first tube was heated at 100 °C for 62 min, and a standard aqueous workup followed. Gas chromatographic analysis showed 70:30 mixture of **24** and **23**. The second tube was heated for 30 min at 125 °C, and a standard aqueous workup followed. Gas chromatographic analysis (6 ft 5% SE 30 on Chromosorb G column) showed ketol **24** and a trace (approximately 5%) of **23** remaining. The infrared and NMR spectra of this major product was identical with those of **24** produced by catalytic hydrogenation of **22**.

Equilibration of 21 and 22. A solution of 30.2 mg of a 2.2:1 mixture of **21** and **22** (obtained from silica gel chromatography of **20**) in 0.6 mL of 0.5 M sodium methoxide in methanol was heated at 100 °C for 60 min. A standard aqueous workup gave a quantitative recovery of ketols **22** and **21**. The 300-MHz NMR showed ketols **22** and **21** in an 89:11 ratio. Similar treatment for 100 min at 125 °C gave the same product ratio.

Exchange Reaction of 22 in Methanol-*d*. A solution of 42.1 mg of **22** in 1 mL of 0.1 M sodium methoxide in CH_3OD (prepared by dissolving 22.2 mg of sodium in 10 mL of CH_3OD) was kept at room temperature for 49 min. The mixture was taken up into ether, washed with D_2O, and dried over $MgSO_4$, and the solvent was removed by rotary evaporator leaving 40.3 mg of product. The 300-MHz NMR of this product showed a decrease in the area of the 2 H multiplet at δ 2.75–2.55 to a 1 H multiplet now centered at δ 2.61. The hydroxyl proton at δ 3.962 also does not appear.

Exchange Reaction of 23 in Methanol-*d*. A solution of 34.9 mg of **2** in 0.7 mL of 0.1 M sodium methoxide in CH_3OD was kept at room temperature for 60 min. After a workup as previously described, the solvent was removed by rotary evaporator (quantitative yield). The 300-MHz NMR of the product showed virtually complete disappearance of the doublet of doublets of doublets at δ 2.903 and also disappearance of the doublet of triplets at δ 2.337.

Exchange Reaction of 24 in Methanol-*d*. A solution of 22.9 mg of **24** in 0.5 mL of 0.1 M sodium methoxide in CH_3OD was kept at room temperature for 70 min. After a workup as described above, the solvent was removed by rotary evaporator leaving 21.8 mg of product. the 300-MHz NMR showed complete exchange of the doublet of doublets at δ 2.64.

An additional 0.7 mL of 0.1 M sodium methoxide in CH_3OH was added to the above residue, and the mixture was heated at 60 °C for 1 hr. A standard workup gave 19 mg of product. The 300-MHz NMR showed a decrease in the area of the 2 H multiplet centered at δ 2.50. The spectrum now showed only a 1 H triplet at δ 2.507. The 1 H signal at δ 2.64 was also not observed.

Exchange Reaction of 30 in Methanol-*d*. A solution of 22.7 of mg **30** in 0.6 mL of 0.1 M sodium methoxide in CH_3OD was kept at room temperature for 42 min. After a workup as previously described, the solvent was removed by rotary evaporator. The 300-MHz NMR showed disappearance of the 1 H doublet of doublets at δ 2.62. The 1 H doublet of triplets at δ 2.40 is collapsed to a 1 H pentuplet.

Exchange Reaction of 31 in Methanol-*d*. A solution of 4.6 mg of **31** in 0.5 mL of 0.1 M sodium methoxide in CH_3OD was kept at room temperature for 45 min. After a workup as previously described, the solvent was removed by rotary evaporator. The 300-MHz NMR showed complete disappearance of the 1 H doublet of doublets at δ 2.70. The 1 H doublet of triplets at δ 2.27 (which overlaps with the 1 H doublet at δ 2.29) is now collapsed to a multiplet. The total area of this region is now 1.41 H (including the 1 H doublet at δ 2.29).

Preparation of 1-Benzoylcyclobutanol, 32. A solution of lithium diisopropylamide, prepared by addition of 4.3 mL of 1.6 M n-butyllithium in hexane to 0.76 g of diisopropylamine in 13 mL of THF at −40 °C, was cooled to −78 °C, and 2.17 g of diethyl-1-(trimethylsiloxy)-1-phenylmethanephosphonate[18] was added dropwise. The mixture was warmed to about −55 °C and then cooled to −100 °C in a frozen methanol–liquid N_2 slurry. A solution of 0.50 g of cyclobutanone in 3 mL of THF was added dropwise, and the mixture was allowed to warm to 0 °C. Water was added, and the mixture was transferred to a separatory funnel with ether and washed with dilute HCl. After the mixture was washed with saturated NaCl solution and dried over $MgSO_4$, the solvents were removed by rotary evaporator. The residue was distilled through an 18-cm Vigreux column, and 1.377 g (81%) of 1-benzoyl-1-(trimethylsiloxy)cyclobutane, bp 67–70 °C (0.05 mm), was collected: NMR ($CDCl_3$) δ 8.1–8.0 (2 H, m), 7.55–7.35 (3 H, m), 2.80–2.65 (2 H, m), 2.40–2.25 (2 H, m), 1.90–1.74 (1 H, m), 1.68–1.50 (1 H, m), −0.08 (9H, s).

A solution of 790 mg of the siloxy ketone obtained above in 9 mL of 10^{-3} M trifluoroacetic acid in methanol was kept at room temperature for 110 min. The solvent was removed by rotary evaporator, and the residue was distilled to give 553 mg (99%) of **32**; bp 91 °C (0.05 mm); NMR ($CDCl_3$) δ 8.2–8.0 (2 H, m), 7.7–7.3 (3 H, m), 3.38 (1 H, b s), 3.0–2.6 (2 H, m), 2.55–1.45 (4 H, m).

Preparation of 2-Phenyl-2-hydroxycyclopentanone, 33. A 550-mg sample of **32** obtained above was chromatographed on 17.5 of silica gel and eluted with increasing percentages of ether in Skelly F beginning with 5% ether. The product **33** (524 mg) eluted with 20% ether and contained no trace of **32**: IR (CCl_4) 1740 cm^{-1} (C=O); NMR ($CDCl_3$) δ 7.32 (5 H, b s), 3.33 (1 H, s), 2.50–2.35 (3 H, m), 2.26–2.13 (1 H, m), 2.11–1.95 (1 H, m), 1.90–1.70 (1 H, m). Anal. Calcd for $C_{13}H_{12}O_2$: C, 82.46; H, 7.55. Found: C, 82.23; H, 7.44.

(20) These chemical shifts for **29** are slightly concentration dependent, as are certain of the other signals for the other ketols described.

(21) The methyl singlet at δ 1.257 is concentration dependent, moving slightly upfield with increasing concentration. Cava[2] has reported a methyl singlet at δ 1.20 along with olefinic signals at δ 6.20 and 5.95 in the product obtained after desilylation and silica gel chromatography of **5**. The spectrum of **31** (the least stable of the isomers **30** and **31**) is most similar to this previously reported[2] product.

Preparation of 7-Benzoylbicyclo[2.2.1]heptan-7-ol, 34. A solution of lithium diethyl-1-(trimethylsiloxy)-1-phenylmethanephosphonate[18] in 8 mL of THF was prepared as previously described from 2.8 mL of 1.6 M *n*-butyllithium, 0.53 g of diisopropylamine, and 1.45 g of diethyl-1-(trimethylsiloxy)-1-phenylmethanephosphonate. After being cooled to −95 °C, a solution of 0.48 g of bicyclo[2.2.1]heptan-7-one in 2 mL of THF was added dropwise. The mixture was warmed to 0 °C and a standard aqueous workup followed with ether extraction. The organic phase was washed with 10% HCl solution and saturated NaCl solution and dried over Mg SO_4. The solvent was removed by rotary evaporator, and the residue was dissolved in 15 mL of 10^{-3} M trifluoroacetic acid in methanol. After the mixture was refluxed for 3 h 15 min, the solvent was removed by rotary evaporator. The crude solid was slurried with Skelly F, and the solvent was decanted. The remaining solid was chromatographed on 25 g of silica gel and eluted with increasing amounts of ether in Skelly F. Solvent removal evaporator gave 239 mg (26%) of **34**: mp 151–3 °C; NMR ($CDCl_3$) δ 8.2–8.1 (2 H, m), 7.55–7.25 (3 H, m), 2.60 (1 H, b s), 2.38 (2 H, m), 2.14 (2 H, m), 1.61 (2 H, m) 1.8–1.2 (4.H, m). Anal. Calcd for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46. Found: C, 77.58; H, 7.31.

Methoxide-Catalyzed Rearrangement of 34. A solution of 51 mg of **34** in 2 mL of 0.5 M sodium methoxide was heated in a sealed tube at 125 °C for 90 min. After a standard aqueous workup and solvent removal by rotary evaporator, 41 mg (81%) of **35** was obtained as an oil: IR (CH_2Cl_2) 3580 (OH). 1723 cm^{-1} (C=O); NMR ($CDCl_3$) δ 7.26 (5 H, s), 3.25 (1 H, br), 2.6–1.2 (10 H, m).

Preparation of 1-Benzoylcyclopentanol, 36. A solution of LDA in 20 mL of THF (from 1.02 g of diisopropylamine and 6.3 mL of 1.6 M *n*-butyllithium in hexane) was treated, as previously described, with 3.19 g of diethyl-1-(trimethylsiloxy)-1-phenylmethanephosphonate. After the mixture was cooled to −85 °C, 1.1 g of cyclopentanone was added dropwise. The mixture was warmed to 5 °C, and ether and water were added. The organic phase was washed with a $KHSO_4$ solution and dried over $MgSO_4$. The solvent was removed by rotary evaporator, and the residue was distilled to give 1.62 g of 1-benzoyl-1-(trimethylsiloxy)-cyclopentane, bp 81–84 °C (0.04 mm). The product was dissolved in 40 mL of 10^{-3} M trifluoroacetic acid in methanol. After 4 h, the solvent was removed by rotary evaporator and the residue was distilled at 105–110 °C (0.08 mm). The distillate was chromatographed on 22 g of silica gel and eluted with increasing amounts of ether in Skelly F. After solvent removal by rotary evaporator, 810 mg of **36**[8e] (42%) was obtained as a clear oil: IR (CCl_4) 1680 cm^{-1} (C=O); NMR ($CDCl_3$) δ 8.2–7.9 (2 H, m), 7.8–7.3 (3 H, m), 3.75 (1 H, s), 2.7–1.6 (8 H, m).

Methoxide-Catalyzed Rearrangement of 36. A solution of 78 mg of **36** in 1 mL of 0.5 M sodium methoxide in methanol was sealed in two tubes. The first tube was heated at 65 °C for 1 h. A standard aqueous workup followed. Infrared analysis showed about 50% conversion to **3**. The second tube was heated at 100 °C for 100 min. A standard aqueous workup followed giving **37**[8e,22] as a clear oil: IR (CCl_4) 1720 cm^{-1} (C=O); NMR ($CDCl_3$) δ 7.44–7.25 (5 H, m), 4.52 (1 H, br s), 3.00 (1 H, m), 2.58–2.30 (2 H, m), 2.10–1.97 (1 H, m), 1.95–1.62 (4 H, m).

Preparation of Mesylate 2. A solution of 47 mg of **3** in 3 mL of CH_2Cl_2 was cooled to −40 °C, and 31 mg of CH_3SOCl[23] was added. Triethylamine (31 mg) was added dropwise, and the mixture was warmed to room temperature. A standard aqueous workup followed with extraction into ether. Gas chromatographic analysis showed about 20% unreacted alcohol **3** along with the sulfinate ester of **3**. The solvent was removed by rotary evaporator. The entire crude mixture was redissolved in 3 mL of CH_2Cl_2, and 35 mg of CH_3SOCl was added followed by 53 mg of Et_3N at room temperature. A standard aqueous workup followed with ether extraction. The excess Et_3N was removed by washing with dilute HCl solution. The ether extract was dried, and the solvent was removed by rotary evaporator. The crude residue was dissolved in 3 mL of CH_2Cl_2, and 65 mg of 85% *m*-chloroperbenzoic acid was added. After 1 h at room temperature, the mixture was taken up into ether, washed with a solution of NaOH, NaI, $Na_2S_2O_3$ in water, and saturated NaCl solution. After being dried over $MgSO_4$, the solvent was removed by rotary evaporator, leaving 64 mg (100%) of mesylate **2** as an oil: NMR ($CDCl_3$) δ 8.07–8.0 (2 H, m), 7.60–7.43 (3 H, m), 2.94 (1 H, m), 2.82 (1 H, doublet of doublets), 2.514 (3 H, s), 2.47 (1 H, m), 2.31 (1 H, m), 2.5 (1 H, m), 1.6–1.3 (4 H, m), 1.20–1.08 (1 H, m).

Solvolysis of Mesylate 2 in Acetic Acid. A solution of 7.7 mg of mesylate **2** in 1.2 mL of HOAc containing 0.05 M sodium acetate and 1% acetic anhydride was kept at 25 °C for 41 h. The mixture was taken up into ether, washed with water and Na_2CO_3 solution, and dried over $MgSO_4$. Solvent removal by rotary evaporatory gave 7 mg of residue. The 300-MHz NMR showed a mixture of the rearranged mesylate **38** and the rearranged acetate **39**[1c] in a 14.6:1 ratio. No starting mesylate **2** remained. **38**: NMR ($CDCl_3$) δ 7.87–7.80 (2 H, m), 7.58–7.42 (3 H, m), 5.110 (1 H, m), 2.579 (3 H, s), 2.45 (1 H, m), 2.20–1.65 (7 H, m), 1.40 (1 H, m).

In a separate experiment, a solution of 9.7 mg of mesylate **2** in 1.5 mL of HOAc (1% acetic anhydride; 0.05 M NaOAc) was kept at room temperature for 5 days and then heated at 100 °C for 1.5 h. After a workup as described above, the solvent was removed by rotary evaporator. The 300-MHz NMR spectrum of the residue showed no unreacted **38** and a mixture of **39**,[1c] **40**,[1c] and **41** in a 9.1:9.6:1 ratio, respectively. Samples of each product were isolated by preparative gas chromatography, and **39**[1c] and **40**[1c] were identified by NMR spectral comparison with authentic samples. **41**: NMR ($CDCl_3$) δ 8.02 (2 H, m), 7.6–7.4 (3 H, m), 6.303 (1 H, d, J = 6 Hz), 6.210 (1 H, doublet of doublets, J = 6, 3 Hz), 3.07 (1 H, br), 2.22 (1 H, m), 1.92 (2 H, m), 1.60–1.10 (3 H, m).

Solvolysis of Mesylates 2 and 38 and *exo*-2-Norbornyl Mesylate[24] in Acetic Acid. Kinetics Procedure. Rates of solvolyses of these mesylates in acetic acid, 0.05 M in sodium acetate, and containing 1% acetic anhydride were monitored by using the sealed technique previously described.[1c,25]

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Registry No. **2**, 95800-13-8; **3**, 34546-65-1; **4**, 42082-94-0; **6**, 82873-54-9; **7**, 95799-88-5; **8**, 95799-89-6; **9**, 34546-64-0; **11**, 82027-16-5; **12**, 95799-94-3; **13**, 95799-95-4; **14**, 95799-96-5; **15**, 82027-24-5; **16**, 95799-97-6; **17**, 95799-98-7; **18**, 95799-99-8; *exo*-**20**, 95799-90-9; *endo*-**20**, 95799-91-0; **21**, 95799-92-1; **22**, 95799-93-2; **22**-*d2*, 95800-04-7; **23**, 34546-71-9; **23**-d_3, 95800-05-8; **24**, 34546-69-5; **24**-d_2, 95800-06-9; **24**-d_3, 95800-07-0; *exo*-**29**, 82873-61-8; *endo*-**29**, 95800-01-4; **30**, 95800-02-5; **30**-α-d_1, 95800-08-1; **31**, 95800-03-6; **31**-α-d_1, 95909-09-4; **32**, 95800-10-5; **33**, 40297-30-1; **34**, 95800-11-6; **35**, 95800-12-7; **36**, 19300-92-6; **37**, 4829-02-1; **38**, 95800-14-9; **39**, 82027-31-4; **40**, 80325-62-8; **41**, 15019-75-7; 1-phenylpropane-1,2-dione, 579-07-7; chlorotrimethylsilane, 75-77-4; cyclopentadiene, 542-92-7; methyl pyruvate, 600-22-6; *endo*-2-acetyl-*exo*-bicylco[2.2.1]heptan-1-ol, 95800-00-3; diethyl 1-(trimethylsiloxy)-1-phenylmethanephosphonate, 31675-43-1; cyclobutanone, 1191-95-3; 1-benzoyl-1-(trimethylsiloxy)cyclobutane, 95800-09-2; bicyclo[2.2.1]heptan-7-one, 10218-02-7; cyclopentanone, 120-92-3; 1-benzoyl-1-(trimethylsiloxy)cyclopentane, 56345-97-2; *exo*-2-norbornyl mesylate, 28627-77-2; *exo*-2-(1-methoxyvinyl)-*endo*-bicyclo[2.2.1]heptan-2-ol, 82027-23-4.

(22) (a) Vedejs, E.; Engler, D. A.; Telschow, J. E. *J. Org. Chem.* **1978**, *43*, 188–96. (b) Corey, E. J.; Kim, C. U. *Tetrahedron Lett.* **1974**, 207–90.

(23) Douglas, I. B.; Norton, R. V. "Organic Syntheses"; Wiley: New York, 1973; Collect. Vol. V, pp 709–15.

(24) Bentley, T. W.; Bower, C. T.; Brown, H. C.; Chloupek, F. J. *J. Org. Chem.* **1981**, *46*, 38–42.

(25) Creary, X. *J. Org. Chem.* **1975**, *40*, 3326–31.