Bicyclo[1.1.1]pentanone. Synthesis, Thermal Chemistry, and Photochemistry†

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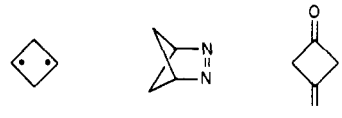
Bicyclo[1.1.1]pentanone (1) has been prepared in two steps, the key reaction being the ozonolysis of 2-phenylbicyclo[1.1.1]pentan-2-ol (6). On heating, 1 undergoes cycloreversion to allylketene (13). The activation parameters and solvent effects for this process suggest that the reaction is concerted and that the transition state is relatively nonpolar. The predominant photochemical pathway for 1 is decarbonylation to bicyclobutane (16). Cycloreversion to 13 is a minor reaction mode. Both the thermal and photochemical results are rationalized by considering the high strain energy and novel geometrical features of 1, and, in the latter case, the unusually high energy of its $^1(n\pi^*)$ state.

Cyclobutanone derivatives have attracted much attention due to their rich thermal chemistry and photochemistry and the insight which their spectral properties offer concerning the nature of the carbonyl functional group.[2] Surprisingly, one of the simplest and perhaps most fundamental of the bicyclic cyclobutanones, bicyclo[1.1.1]-pentanone (1), has not been reported previously. This

1

highly strained, symmetrical ketone might be expected to display novel spectroscopic, thermal, and photochemical properties due to its severe ring constraints.

Our own interest in 1 arose from its potential as a precursor to the localized triplet biradical cyclobutane-1,3-diyl (2). In an earlier study, we prepared[3] 2,3-diazabicyclo-

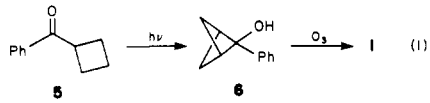


2 3 4

[2.1.1]hex-2-ene (3) but found that photolysis of 3 at 8.5 K in the cavity of an ESR spectrometer did not produce a signal corresponding to 2.[4] We had also performed ab initio calculations[5] that predict a triplet ground state for 2—a necessary criterion for success in such ESR experiments. Therefore, an alternative photochemical precursor to 2 was sought. We chose 1 by analogy to Dowd's successful use of 3-methylenecyclobutanone (4) as a precursor to the trimethylenemethane biradical.[6]

We describe herein a simple synthesis of 1 and characterization of its spectral, thermal, and photochemical properties. Although 1 has not proven to be a viable ESR precursor to 2, its chemical and spectroscopic behavior sheds new light on several aspects of cyclobutanone chemistry.

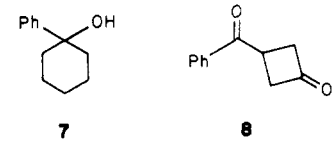
Synthesis and Spectroscopic Characterization. Ketone 1 was prepared by using a simple, two-step sequence (eq 1). Photolysis of commercially available cyclobutyl phenyl ketone (5) using the method of Padwa[7] produced 2-phenylbicyclo[1.1.1]pentan-2-ol (6). Ozono-



5 6 (1)

lysis[8] of 6 in CH_2Cl_2 afforded 1 as a colorless oil after purification by azeotropic distillation and preparative gas chromatography. GC analysis of the reaction mixture revealed that the yield of 1 was ca. 8%. Losses during purification were unavoidable, due to the high volatility of 1, and the isolated yield was 4%. We anticipate that this procedure will be more useful for the preparation of substituted bicyclopentanones, for which isolation should be less problematical. Despite the low yield, the brevity of the overall synthesis makes useful quantities of 1 easily available.

For comparison, ozonolysis of 1-phenylcyclohexanol (7) under the same conditions resulted in a 67% GC yield of cyclohexanone, suggesting that ring strain in 6 or 1 also contributes to the low yield of 1. Alcohol 7 can also be



7 8

oxidized to cyclohexanone by using ruthenium tetraoxide.[9] We therefore attempted oxidation of 6 with ruthenium tetraoxide using Sharpless' procedure.[10] However, a much lower yield of 1 was observed, and 3-oxocyclobutyl phenyl ketone (8) and benzoic acid were observed among the products. The formation of these products is consistent with the above suggestion that the low yield of 1 is probably due in part to attack of the oxidizing agent on the strained ring system.

† Contribution No. 7022.

(1) (a) NSF Predoctoral Fellow, 1982-1985. (b) Fellow of the Alfred P. Sloan Foundation, 1983-1985.

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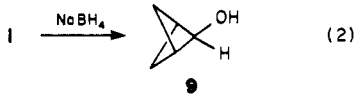
Structure proof for 1 rests on the range of spectroscopic data discussed below, exact mass determination and chemical behavior. In particular, reduction of 1 with $NaBH_4$ (eq 2) in methanol gives a product whose ^1H NMR spectrum is identical with that reported by Wiberg[11] for bicyclo[1.1.1]pentan-2-ol (9).



(2)

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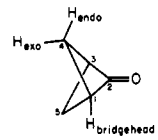
Ketone 1 is quite strained, as demonstrated by the infrared carbonyl stretch at 1810 cm^{-1}. This value is intermediate between that of cyclobutanone (1788 cm^{-1})[12] and cyclopropanone (1813 cm^{-1}).[13] In the closely related molecule, tricyclo[2.1.0.$0^{2,5}$]pentanone (10), the carbonyl

10 11 12

stretch appears at 1775 cm^{-1}.[14] This suggests that the ketone moiety in 1 is actually more strained than that in 10, presumably because the carbonyl C–C–C angle is larger in 10 due to the presence of the constrained bicyclobutane skeleton.

The ^1H NMR spectrum of 1 in $CDCl_3$ exhibits a sharp singlet at 3.01 ppm ($H_{bridgehead}$) and slightly broadened singlets at 1.80 ppm (H_{exo}) and 1.49 ppm (H_{endo}). The



assignment of the exo and endo protons was based on comparison with the methylene protons in bicyclo[1.1.1]pentane (11, 1.84 ppm)[15] and the observation that the endo protons are in the anisotropic shielding region of the carbonyl.[16]

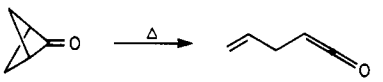
The ^{13}C NMR spectrum has resonances at 189 ppm (C_2), 55 ppm (C_1), and 36 ppm (C_4). The carbonyl ^{13}C singlet appears at higher field than normal for ketones, but the same observation has been reported for other polycyclic ketones,[17] including 4,5-bis(methylene)bicyclo[1.1.1]pentanone (12), for which the carbonyl peak appears at 180.7 ppm.[18]

The ultraviolet spectrum of 1 shows an unusually high energy $n\pi^*$ transition for an alicyclic ketone. The band shows no vibrational structure and has λ_{max} 247 nm (ϵ_{max} 14) in *n*-pentane. This is, to our knowledge, the shortest wavelength $n\pi^*$ absorption reported for a saturated aliphatic ketone. Such a blue shift is not characteristic of strained ketones, as shown by the λ_{max} of 279 nm for cyclobutanone[12] and 310 nm for cyclopropanone.[13]

In an effort to understand the origin of this blue shift, we recorded the photoelectron spectrum of 1.[19] The first ionization is well-separated from other bands and displays a vertical ionization potential of 9.51 eV. The observed IP for 1 is slightly lower than the IP for acetone (9.70 eV),[20] and thus the high-energy $n\pi^*$ transition does not result from an unusually low-lying n orbital. At present we feel that this effect is most likely due to adverse electron repulsions in the $n\pi^*$ state between the electron that is formally in a π^* orbital and the endo C–H bonds, as these bonds protrude directly into the region of the π^* orbital.

We attempted to observe emission from 1 in 2-methyltetrahydrofuran (degassed) at both room temperature and at 77 K. Using an excitation wavelength of 247 nm, no emission was observable from 247 to 360 nm. This negative result is consistent with Lee's observation that the excitation spectrum of cyclobutanone drops to zero for excitation wavelengths less than 290 nm.[21]

Thermal Chemistry. Cyclobutanones characteristically undergo thermal [2 + 2] cycloreversions to give ketene and olefin products.[22] In 1, there are four degenerate modes for cycloreversion, all of which lead to allylketene (13) (eq 3). Cycloreversion is indeed observed and proceeds much more readily than that for any other cyclobutanone of which we are aware.

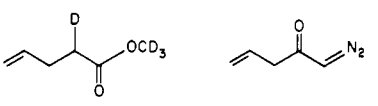


(3)

1 13

Thermolysis of 1 in degassed benzene-d_6 solution at 80 to 122 °C yielded four major products of long (relative to 1) GC retention times and a series of minor products with progressively longer retention times. GC–MS analysis clearly indicates that all of these products are of high molecular weight relative to 1. Molecular weights corresponding to trimer and tetramer were observed. The ^1H NMR spectrum of the mixture is dominated by a strong, characteristic allyl pattern with signals at 2.1, 4.9, and 5.5 ppm, and the ^{13}C spectrum supports the presence of allyl groups with peaks at 28, 116, and 136 ppm. These data are consistent with the formation of 13 followed by oligomerization.

Strong support for the formation of 13 was obtained from the thermolysis of 1 at 100 °C in methanol-d_4.[23] Methyl-d_3 4-pentenoate-2-*d* (14) was obtained in nearly



14 15

quantitative yield, presumably by trapping of 13 with solvent. In addition, we prepared and studied the decomposition of 1-diazo-4-penten-2-one (15), which should decompose thermally or photochemically via the Wolff rearrangement[24] to yield 13. Indeed, photolysis of 15 in

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(17) (a) Maier, G.; Pfriem, S.; Schaefer, U.; Malsch, K. D.; Matusch, R. *Chem. Ber.* **1981**, *114*, 3965–3987. (b) Hoye, T. R.; Martin, S. J.; Peck, D. R. *J. Org. Chem.* **1982**, *47*, 331–337.
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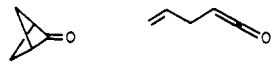
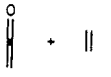
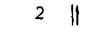
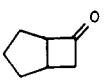
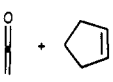
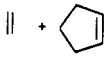
(23) A small amount of sodium bicarbonate was added to inhibit ketalization.

Table I. Activation Parameters for Cyclobutanones and Cyclobutanes

compd	products	E_a, kcal/mol	log A	ref
		28.6	12.9	
		49.0	15.3	25
		51.9	14.6	22c
		62.5	15.6	26
		48.6	14.2	27
		60.7	14.8	28

benzene-d_6 yielded several products including, as 60% of the mixture, two components which coeluted on two different capillary GC columns with two of the major products obtained from 1. Although decomposition of **15** does not provide the identical mixture obtained from **1**, the different temperature and mode of generation of **13** can explain this difference. Thus, the dominant, if not exclusive, thermal reaction mode of **1** is cycloreversion to **13**.

The kinetics of the thermal decomposition of 1 in C_6D_6 followed strictly first-order behavior through at least 2 half-lives, as monitored by multiple ^1H NMR integration. The activation parameters, obtained over a 40° temperature range, are given in Table I along with others selected for comparison. Most cyclobutanones require temperatures in excess of 180 °C for measurable decomposition, and nearly all of the studies reported in the literature have been done in the gas phase.[22] In contrast, **1** decomposes readily around 100 °C, allowing convenient study in the solution phase. In order to make our solution-phase results[29] more amenable to comparison with the earlier studies, however, we carried out the gas-phase decomposition of 1 at 100 °C and approximately 0.2 torr. The reaction rate was comparable to solution-phase decomposition at the same temperature, and the same products were observed, though in different relative yields. This variation in product composition between solution- and gas-phase experiments is not surprising, given that oligomerization is involved.

Thermal decomposition of cyclobutanones has been postulated to proceed by a polar, concerted mechanism,[2c] in contrast to the decomposition of cyclobutanes, which is thought to involve biradical intermediates.[28,30] In order to address the question of polarity in the transition state, the decomposition of 1 was carried out in acetonitrile-d_3 and methanol-d_4 at 100 °C. The decomposition proceeded 1.8 times faster in acetonitrile and 7.7 times faster in methanol than it did in benzene at that temperature.[31] In view of these relatively modest rate enhancements,[32] we believe that the transition state is only weakly polar.

This conclusion seemingly contradicts the findings of Egger[2c] and of Frey[33] that charge stabilizing substituents on C_3 of cyclobutanone markedly enhance the rate of gas-phase thermal decomposition, indicating a polar transition state. These results need not be contradictory, however, if we accept that substitution of charge stabilizing groups on C_3 of cyclobutanone can induce polar character in the transition state, and in doing so stabilize it. In the absence of such substituents, the reaction proceeds through a relatively nonpolar transition state.

In distinguishing between biradical and concerted pathways, activation parameters can be very useful.[34] Log A is generally slightly lower for cyclobutanones than for the corresponding cyclobutanes (Table I), indicating more order in the transition state for cyclobutanones relative to cyclobutanes. This trend is especially pronounced in the case of 1. The concerted transition state should have a highly ordered, twisted structure to provide good overlap in the allowed $\sigma 2s + \sigma 2a$ process.[30a] This is consistent with a low log A value. In contrast, a biradical path would appear inconsistent with such a small log A value. Note that the contribution to log A due to solvent reordering in the transition state is expected to be small, given the weakly polar nature of the reaction.

The activation energy is also inconsistent with a two-step process for 1. If we assume a biradical mechanism for the cycloreversions of both 1 and 11, then we must account for the fact that the activation energy for 1 is 20 kcal/mol less than that for 11. The difference in intrinsic bond dissociation energies can account for at most 5 kcal/mol of this difference.[35] It seems unlikely that the remaining difference of 15 kcal/mol could be explained by differences in strain energies between 1 and 11 or between their respective transition states. In fact, we have carried out MNDO calculations on both 1 and 11 and found the strain energies[36] to be nearly identical.[38] We thus conclude that the much lower E_a for decomposition of 1 vs. 11 is due to stabilization of the transition state for 1 by virtue of the fact that it is a concerted process.

Photochemistry. The photochemistry of cyclic ketones has been widely studied.[2a,b,40] As a consequence of their greater strain energy, cyclobutanones exhibit photochemistry[2a,b,d] which differs markedly from their higher homologues. Structure 1 is a highly strained cyclobutanone, and its photochemistry is similar in most respects to that of other cyclobutanones. The observed differences may be explained in terms of the higher strain energy, the higher

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(28) Ellis, R. J.; Frey, H. M. *J. Chem. Soc.* **1964**, 4184–4187.
(29) For another solution phase study, see: Jones, G., II; Zalk, S. A. *Tetrahedron Lett.* **1973**, 4095–4098.
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(31) Although the product mixtures vary with solvent, the rate comparisons are still valid, since the rate-determining step in all three solvents is presumably the formation of **13**.
(32) Gassman, P. G. *Acc. Chem. Res.* **1971**, *4*, 128–136.
(33) Frey, H. M.; Smith, R. A. *J. Chem. Soc., Perkin Trans. 2* **1977**, 2082–2084.
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(36) Strain energies were calculated as the difference between the heats of formation provided by MNDO and Benson group values.[37]
(37) Reference 35b, pp 272–275.
(38) Although MNDO calculations on such strained molecules could be fairly inaccurate in an absolute sense,[39] they should be acceptable for discerning such trends among closely related molecules.
(39) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4907–4917.
(40) (a) Weiss, D. S. *Org. Photochem.* **1981**, *5*, 347–420. (b) Chapman, O. L.; Weiss, D. S. *Org. Photochem.* **1973**, *3*, 197–288. (c) Yates, P. *Pure Appl. Chem.* **1968**, *16*, 93–113. (d) Srinivasan, R. *Adv. Photochem.* **1963**, *1*, 83–113.

energy of the $n\pi^*$ state, and geometric considerations.

Several processes are generally observed in cyclobutanone photochemistry, all of which are thought to be initiated by α-cleavage to an acyl alkyl biradical. Decarbonylation, fragmentation to ketene plus olefin, and ring expansion to oxacarbene are generally observed from cyclobutanones, whereas intramolecular disproportionation (ketene and enal) products are usually only observed in larger ring ketones.[2a,b]

Photolysis of 1 in cyclohexane-d_{12} with Vycor-filtered light at room temperature (eq 4) affords bicyclo[1.1.0]butane (16) in ca. 70% yield, along with a small amount (1–2%) of cyclobutene (17). A characteristic allyl pattern was observed in the ^{1}H NMR spectrum of the mixture and a white solid was formed; these products have not been identified, but they are likely to have been derived from the ketene 13 (see below).

16 17 (4)

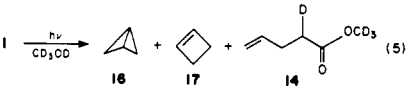
Examination of the photolysis results shows that decarbonylation is by far the most important process for 1. The yield of decarbonylation product (16) is much higher than is normally observed for saturated cyclobutanones,[2a] and the yields of cycloreversion and ring expansion products are correspondingly lower.

These observed relative yields can be rationalized in terms of energetic and geometric considerations. First, decarbonylation is generally more important for ketones that are highly strained,[41] and 1 is one of the most strained cyclobutanones which has been studied. Second, the $n\pi^*$ absorption of 1 is about 14 kcal/mol higher in energy than for most ketones. This extra energy is about the same as the estimated barrier to loss of CO from the first-formed acyl alkyl biradical,[42] in this case 18, and could thus greatly accelerate this process.

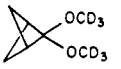

18

In addition, a pathway expected to compete with decarbonylation, β-cleavage to give cycloreversion product 13, may be disfavored by geometric considerations. In the optimum geometry for cleavage of 1,4-biradicals, the radical p orbitals are parallel to the breaking σ bond,[43] allowing for high overlap in the transition state. However, the alkyl radical p orbital in 18 is constrained by the four-membered ring to remain nearly perpendicular to the breaking σ bond, unless the ring becomes severely twisted. This effect should serve to lower the relative yield of cycloreversion products.

That cycloreversion is occurring in 1 was suggested by the allyl resonances in the product mixture. To confirm this result, we carried out a photolysis of 1 in methanol-d_4 in the presence of sodium bicarbonate (eq 5). This leads to a mixture of 16 and 17 in yields comparable to the cyclohexane experiment, and also 14 (15%). The presence of 14 provides strong evidence for the formation of 13. Sodium bicarbonate is necessary to consume acidic products which are formed during the photolysis. In the absence of base, a substantial amount of the dimethyl ketal 19 is formed, and the bicyclobutane product (16) undergoes



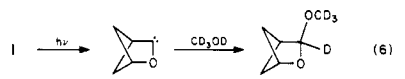
16 17 14 (5)



19

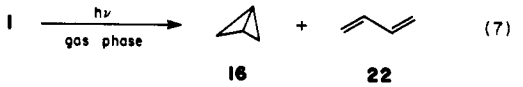
acid-catalyzed addition of methanol.[44] In the presence of bicarbonate, the formation of 19 is completely inhibited,[45] but small amounts of bicyclobutane methanolysis products are still observed.

A striking feature of the methanolic photolysis experiment is the absence of 3-(methoxy-d_3)-2-oxabicyclo[2.1.1]hexane-3-d (20), which would be formed by trapping of the oxacarbene 21 by the solvent (eq 6). The ring expansion of cyclic ketones to cyclic acetals is relatively rare for five-membered and larger ring ketones but is general for cyclobutanones.[46] Moreover, the yield of ring-expanded acetal is generally higher for ketones with more strain.[46b] The absence of ring expansion in the case of 1 may be rationalized by noting that the oxacarbene 21 should be more strained than a typical cyclobutanone-derived oxacarbene and that ring expansion must compete with an especially favorable decarbonylation (see above).



21 20 (6)

Gas-phase photolysis of 1 at room temperature gives mixtures of 16 and 1,3-butadiene (22) in a ratio that depends on pressure (eq 7). No allyl signal was observed in the ^{1}H NMR spectrum, but a transparent film on the inside of the tube was observed. It seems likely that this film arises from polymerization of 13.



16 22 (7)

The formation of 22 in the gas-phase photolysis, but not in solution phase, suggests that this product derives from vibrationally activated bicyclobutane. The formation of 22 has been observed from direct heating of 16[47] and also from chemically activated 16 produced in the gas-phase thermolysis of azoalkane 3.[48,49] Thus it is not surprising that 22 is formed in photolysis of 1, and only in the gas phase, where collisional deactivation is slow. A control photolysis of 16 under the same conditions showed that 22 is not formed from secondary photolysis. We cannot rule out an alternative route to 22 involving secondary photochemical CO extrusion from ketene 13 to give a carbene that can rearrange to 22, although one would not anticipate significant pressure dependence in this route.

Finally, we must consider the formation of cyclobutene (17) as a very minor product in the photolysis of 1. One possibility is the formation of cyclobutane-1,3-diyl (2), which undergoes mainly closure to 16, with a small fraction undergoing a 1,2-hydrogen shift to give 17. Cyclobutene

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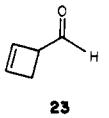
was *not* observed in the direct photolysis of azoalkane **3**,[4] which also yields **16**. Additionally, thermolysis of **3** in solution produces biradical **2**, but only ring closure to **16** ensues—no cyclobutene is formed.[3,48] This lack of a hydrogen shift in **2** has been rationalized as resulting from a stereoelectronic effect.[49] However, the high strain energy of **1** and the large amount of energy absorbed (247 nm = 116 kcal/mol) lead to a very large amount of excess vibrational energy in the fragmentation products. The formation of **17** from **2** could be the result of such chemical activation, although such processes are quite rare in solution.

Alternatively, the acyl alkyl biradical **18** could undergo intramolecular hydrogen abstraction to give 2-cyclobutenecarboxaldehyde (**23**) which then decarbonylates



23

photochemically to give **17**. Analogous enal products are common from larger ring ketones,[40a,b] but are very rare from cyclobutanones,[2a] presumably because the hydrogen abstraction involves a strained four-membered ring transition state. Once again, however, the extra vibrational energy in **18** could allow for a small yield of this product. Decarbonylation of **23** might be expected to proceed readily, in that cyclobutane is a major product in the photolysis of cyclobutanecarboxaldehyde.[50] In **23**, decarbonylation could be further favored by the formation of a stabilized radical, 2-cyclobuten-1-yl, and by the fact that decarbonylation of aldehydes generally proceeds with higher efficiency under shorter wavelength photolysis.[51]

A third possibility is the formation of butadiene (**22**), which undergoes secondary photolysis to **17**. This possibility, however, was ruled out by a control photolysis of **22** in cyclohexane-d_{12}. The conversion of **22** to **17** was found much too inefficient to explain the formation of **17** from photolysis of **1**.

Conclusion. Useful quantities of ketone **1** can be conveniently prepared in only two steps from commercially available material. Because of its high strain energy, **1** is much more thermally labile than typical cyclobutanones. The dominant thermal pathway is a concerted, $\sigma 2s + \sigma 2a$ cycloreversion to allylketene (**13**), which then oligomerizes. The transition state for this process contains little or no polar character. Photolysis of **1** results mainly in decarbonylation to produce bicyclobutane (**16**). A minor pathway is cycloreversion to **13** but no ring expansion (oxacarbene) products are observed.

Experimental Section

A. General Methods. ^{1}H NMR spectra were recorded on a Varian EM-390 spectrometer. Fourier transform NMR were recorded using either a JEOL FX-90Q spectrometer (^{1}H and ^{13}C) or a Bruker WM-500 spectrometer (^{1}H). IR spectra were recorded on a Beckman Model 4240 IR spectrophotometer. UV spectra were recorded using a Beckman Model 25 spectrophotometer. Mass spectra were obtained by the Midwest Center for Mass Spectrometry at the University of Nebraska, Lincoln, NE, or by the Caltech Analytical Facility. The PE spectrum was recorded using a He I UV spectrometer which was built at Caltech and is described in the literature.[52] Fluorescence spectroscopy was performed using a fluorimeter which has been previously described.[53] Analytical gas chromatography was performed on a Hewlett-Packard 5840A chromatograph equipped with a flame ionization detector. Retention times are reported for a 30 m × 0.329 mm DB-17 25-μm film on fused silica column with H_2 carrier gas, linear velocity 42 cm/s, and an oven temperature program starting at 50 °C for 2 min, increasing at 10°/min until reaching and remaining at 200 °C. Preparative gas chromatography was performed on a Varian Aerograph Model 90-P chromatograph with a thermal conductivity detector.

B. Synthesis. 2-Phenylbicyclo[1.1.1]pentan-2-ol (6). The method of Padwa and co-workers[7] was used, except that the crude product was purified by flash chromatography[54] on 70–230-mesh silica gel using a 3:1 mixture of pentane and ethyl acetate, yielding 3.6 g of **6** from 10 g of **5** (Aldrich).

Bicyclo[1.1.1]pentanone (1). A 1000-mL three-necked round-bottomed flask was charged with 3.6 g (22.5 mmol) of **6** and 600 mL of dichloromethane and equipped with magnetic stirring and a dry ice/acetone condensor with drying tube. The flask was cooled with an ice bath and ozone was bubbled through the solution at about 0.8 mmol/minute by using a gas dispersion tube and paraffin film to close the opening around the dispersion tube. The ice and dry ice were regularly replenished and the ozone flow was stopped after 6 h. The mixture was allowed to stir overnight at room temperature and was then filtered through a pad of silica gel. All but about 25 mL of the solvent was removed by careful atmospheric distillation using a 12-cm vacuum-jacketed Vigreux column. The solution was transferred to a 50-mL flask, and more solvent was removed to leave about 10 mL of solution. The product was then purified by azeotropic distillation as follows. A 500-mL flask was installed as receiver and 10 mL of pentane was added to the product solution via an addition funnel. Approximately 10 mL of distillate was collected, followed by addition of another 10 mL of pentane, and distillation. This process was repeated 24 times or until none of the product **1** remained in the residue, as determined by capillary GC (t_R 3.4 min). Dichloromethane (90 mL) was added to the combined distillate and the mixed solvent was removed by distillation using the vacuum-jacketed column, stopping when the distillation temperature rose from 30 °C to 32 °C. The solution was transferred to a smaller flask and 1 volume of dichloromethane was added for every 3 volumes of solution. Distillation was continued in this manner to concentrate the product solution to about 3 mL. If any of the distillates contained any of the product (by GC), then they were concentrated as above. The resulting solutions were further purified by preparative gas chromatography (25% DEGS on Chromosorb WAW-DMCS, 60/80 mesh, 5 ft × $^3/_8$ in., 80 °C, 60 mL/min He, t_R 14 min), using a glass coil with vacuum stopcocks in dry ice/acetone to collect the product (collection efficiency, 74%). (Once the coil contained some of the product, better efficiency was obtained by using liquid nitrogen.) The product (~70 mg, 4%) was then vacuum transferred from the collection coil in dry ice/CCl_4 to a small bulb with a vacuum stopcock in liquid N_2 for storage (in freezer): ^{1}H NMR ($CDCl_3$) δ 1.49 (s, H_{endo}), 1.80 (s, H_{exo}), 3.01 (s, $H_{bridgehead}$); ^{13}C NMR ($CDCl_3$) δ 35.61 (C_4, $^1J_{CH}$ = 152 Hz), 55.10 (C_1, $^1J_{CH}$ = ~173 Hz), 188.64 (C_2) (for comparison, **11**;[15] $^1J_{C(1)-H}$ = 164 Hz, $^1J_{C(2)-H}$ = 144 Hz); IR ($CDCl_3$) 3030, 3002, 2900, 1810, 1791, 1758, 1185 cm^{-1}; UV (*n*-pentane) λ_{max} 247 nm (ϵ 14); mass spectrum (EI), *m/e* (relative intensity) 82 (100), 54.8 (29), 54 (41), 53 (42), 39 (48), 28 (85); exact mass calcd for C_5H_6O 82.04186, found 82.04194.

Ozonolysis of 1-Phenylcyclohexanol (7). 1-Phenylcyclohexanol (100 mg, 0.57 mmol, Alfred Bader Chemicals) was dissolved in 50 mL of dichloromethane in a 100-mL round-bottomed flask. The solution was cooled in an ice bath and ozone (~0.8 mmol/min) was bubbled through the solution. After 2.5 h, the ozone flow was stopped and the solution allowed to warm. Cyclohexanone was identified as the major product by ^{1}H NMR, TLC, and GC; yield 67% (by GC).

RuO_4 Oxidation of 6. Oxidation of 130 mg (0.81 mmol) of **6** was performed by using the ternary solvent ($CCl_4/CH_3CN/H_2O$) method of Sharpless.[10] Starting material was gone after ~1 day, although **1** was not detected by TLC. The reaction was worked

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up after 3 days, yielding ~2% of 1 (by GC). The product mixture (in CH_2Cl_2) was separated into acidic and neutral fractions by extraction with aqueous NaOH. The acidic fraction was found by ^1H NMR to consist of benzoic acid and a material which we tentatively assigned the structure of cyclobutanecarboxylic acid in a ratio of about 1:1. The neutral fraction was analyzed by ^1H NMR and GC and found to contain a 1:1 ratio of **5** (t_R 13.4 min) and 3-oxocyclobutyl phenyl ketone (**8**, t_R 16.5 min). A small amount of **5** was present in the starting material as an impurity, though probably not enough to account for the **5** observed in the product mixture. Further purification of **8** by flash chromatography (pentane/ethyl acetate, 4:1) gave a pale yellow oil: ^1H NMR ($CDCl_3$) δ 3.4 (m, 4 H), 4.0 (p, 1 H), 7.5 (m, 3 H), 8.0 (dd, 2 H); IR ($CDCl_3$) 3060, 2910, 1792, 1725, 1682, 1580, 1450, 1348, 1225, 1100 cm^{-1}; mass spectrum (EI), *m/e* (relative intensity) 174 (2), 146 (35), 113 (12), 111 (25), 105 (100), 77 (48), 51 (32).

Reduction of 1 to Bicyclo[1.1.1]pentan-2-ol (9). A solution of 2.5 mg (0.030 mmol) of **1** in 2 mL of pentane (from azeotropic distillation) was placed in a 25-mL round-bottomed flask with 10 mL of methanol and stirred at 0 °C. A 2.2-mg (0.058 mmol) sample of sodium borohydride (Aldrich) was added. After 20 min, 8 μL of 3 N hydrochloric acid was added. All but 1 mL of the solvent was removed by distillation and 10 mL ether was added to the concentrate. The ether solution was washed with water, saturated sodium chloride, again with water, and then dried over sodium sulfate for 1 h. The solution was filtered and the filtrate concentrated to 2 mL by distillation. The concentrate was purified by preparative gas chromatography under the same conditions as for **1**, except that a flow rate of 150 mL/min was used; **9** had a retention time of 20 min. We obtained 0.6 mg (0.007 mmol, 23% yield) of **9**, which exhibited a ^1H NMR spectrum identical with the literature spectrum.[11]

1-Diazo-4-penten-2-one (15). The method of Smith and coworkers[55] was followed, except that the product was purified by flash chromtography by using pentane/ether (2:1): ^1H NMR (C_6D_6) δ 2.6 (d, 2 H), 4.1 (s, 1 H), 4.8 (m, 2 H), 5.7 (m, 1 H).

C. Thermal Decomposition Studies. All solution-phase thermolyses were performed with samples in degassed (five freeze–pump–thaw cycles) 5-mm NMR tubes. A well-insulated silicone oil bath with a Bayley Model 253 proportional temperature controller was used. The temperature was monitored accurately by using an iron–constantan thermocouple connected to a digital voltmeter.

Decomposition of 1. (a) Kinetics. A stock solution of 24 mg of **1** in 10 mL of benzene-d_6 was prepared and divided into several tubes. The decomposition kinetics were studied in the temperature range between 80 and 122 °C and the reaction progress was monitored by 90-MHz ^1H NMR spectroscopy, using several integrations over the signals at 0.8 (H_{endo}) and 1.2 ppm (H_{exo}) and the benzene peak as reference. The signal from the bridgehead hydrogens (2.4 ppm) was not used due to interference from products. The reaction was followed through 2 to 2.5 half-lives at each temperature. The rate data were analyzed by using a linear least-squares method which incorporates error analysis.[56] All rate plots gave correlation coefficients higher than 0.996, and the Arrhenius and Eyring plots had correlations of 0.9999. Two experiments using samples made from different stock solutions (different concentrations) were included, since no decrease in correlation resulted from this inclusion. Errors represent two standard deviations. Rate constant $\times 10^5$ s^{-1} (T, °C): 1.52 ± 0.06 (79.89 ± 0.12), 3.11 ± 0.09 (86.05 ± 0.05), 4.82 ± 0.27 (89.66 ± 0.10), 6.07 ± 0.2 (92.37 ± 0.03), 11.7 ± 0.8 (98.18 ± 0.03), 21.3 ± 1.0 (104.47 ± 0.04), 40.9 ± 2.2 (110.90 ± 0.08), 122 ± 4 (122.34 ± 0.16). E_a = 28.57 ± 0.28 kcal/mol, log A = 12.87 ± 0.16, $\Delta H^{\ddagger}$ = 27.82 ± 0.28 kcal/mol, $\Delta S^{\ddagger}$ = −2.09 ± 0.76 eu.

In order to rule out the possibility of acid catalysis in the thermolysis experiments, the disappearance rate at 100.47 ± 0.08 °C was measured for a sample of **1** in C_6D_6 with 0.2 equiv of 2,6-lutidine. The measured rate, (15.6 ± 2.1) $\times 10^{-5}$ s^{-1}, is within experimental error of the expected rate of 14.4 $\times 10^{-5}$ s^{-1}.

The rate of thermal decomposition was also measured for 3 mg of **1** in acetonitrile-d_3 at 100.50 ± 0.04 °C. The rate plot gave a correlation coefficient of 0.9995 and a rate constant of (26.0 ± 0.8) $\times 10^{-5}$ s^{-1}. The rate constant expected for thermolysis of **1** in benzene-d_6 at this temperature is 14.4 $\times 10^{-5}$ s^{-1}, giving a solvent rate enhancement of 1.8 times for CD_3CN relative to C_6D_6.

The decomposition rate was also measured for 4 mg of **1** in methanol-d_4 with 10 mg of $NaHCO_3$ at 99.98 ± 0.08 °C. The measured rate was (106 ± 7) $\times 10^{-5}$ s^{-1} with a correlation coefficient of 0.9994. The expected rate at this temperature with benzene as solvent is 13.7 $\times 10^{-5}$ s^{-1}. The rate enhancement is thus 7.7 times for methanol relative to benzene.

(b) Products. (i) Thermolysis of **1** in C_6D_6: ^1H NMR (integration relative to initial starting material) δ 2.1 (m, 3.3 H) 4.9 (m, 1.8 H), 5.5 (m, 0.9 H); ^{13}C NMR δ 28, 116, 136; GC t_R, min (relative area, GC–MS M^+ if found) 7.4 (16), 10.2 (13), 11.0 (36), 16.8 (35, 246 amu), 22.1 (trace, 328 amu). Trace amounts of several longer t_R components were also detected. The GC yields are given for the 98 °C experiment; the others varied by up to 5%. (ii) Thermolysis of **1** in CD_3CN: ^1H NMR δ 2.4 (m, 3.1 H), 3.6 (s, 0.2 H), 5.0 (m, 1.8 H), 5.8 (m, 0.9 H); GC t_R, min (relative area) 3.4 (3), 3.5 (41), 7.4 (4), 10.2 (28), 11.0 (24). (iii) Thermolysis of **1** in CD_3OD (methyl-d_3 4-pentenoate-2-*d* (14)). ^1H NMR δ 2.3 (m, 2 H), 2.4 (m, 1 H), 4.98 (d, 1 H), 5.05 (d, 1 H), 5.8 (m, 1 H); t_R 3.5 min, yield 88.5%. An authentic sample of methyl-d_3 4-pentenoate was made by mildly heating 4-pentenoic acid in CD_3OD with 1 drop DCl in D_2O for several hours. The authentic sample had t_R and NMR spectral characteristics identical with the photolysis product, except for the expected differences in integration and coupling constants due to protium substitution. No evidence for divinyl ketone, a possible side product, could be seen by NMR, and there was no evidence for oligomers of any sort by GC. (iv) Gas-phase thermolysis of **1**: 1.3 mg (0.016 mmol) of **1** was thermolyzed at 100 °C in a 2-L bulb (~0.2 torr) for 4 h. Benzene-d_6 (0.5 mL) was vacuum transferred into the bulb and the solution pipeted into an NMR tube. By GC, 41% of the starting material was left, giving an approximate rate constant of 6 $\times 10^{-5}$ s^{-1}; ^1H NMR δ 1.9 (m ~1 H), 2.7 (m, ~2 H), 4.9 (m, 2 H), 5.7 (m, ~1 H); GC t_R, min (relative area) 7.4 (16), 10.2 (81), 11.0 (3).

Decomposition of 15. (a) Photolysis. **15** (0.8 mg) in 0.5 mL benzene-d_6 in an NMR tube was photolyzed under N_2 for 2.5 h by using Pyrex-filtered light: ^1H NMR δ 2.2 (m, ~3 H), 4.9 (m, ~2 H), 5.5 (m, ~1 H); GC t_R, min (relative area) 4.5 (16), 6.6 (14), 10.2 (25), 11.0 (35), 14.2 (10). The components with t_R 10.2 and 11.0 coeluted on both DB-5 and DB-17 capillary columns with the corresponding components in a sample from thermolysis of **1**.

(b) Thermolysis. **15** (1.5 mg) in benzene-d_6 was thermolyzed at 119.3 °C for 2 h: ^1H NMR δ 2.0 (m, 0.5 H), 2.2 (m, 0.5 H), 2.6 (m, 0.9 H), 4.6 (s, 0.3 H), 4.9 (m, 2.6 H), 5.5 (m, 1.3 H); GC t_R, min (relative area) 6.6 (2), 6.8 (4), 8.5 (8), 10.9 (86). It seems likely that the major product arises from cycloaddition of **13** and **15**.[57]

D. MNDO Calculations. The geometry of **1** was completely optimized (retaining C_{2v} symmetry), giving C_1–C_2 = 1.552 Å, C_1–C_4 = 1.576 Å, C_2–O = 1.205 Å, C_1–H = 1.082 Å, C_4–H_{endo} = 1.101 Å, C_4–H_{exo} = 1.100 Å, $\angle C_1$–C_2–C_3 = 76.9°, $\angle C_1$–C_4–C_3 = 75.6°, $\angle$O–C_2–C_4 = 119.0°, $\angle$H–C_4–H = 107.9; ΔH_f = 31.93 kcal/mol, IP = 10.31 eV. The geometry of **11** was optimized (retaining D_{3h} symmetry), giving C–C = 1.573 Å, C_1–H = 1.083 Å, C_2–H = 1.101 Å, $\angle C_1$–C_2–C_3 = 74.1°, $\angle$H–C–H = 107.6°; ΔH_f = 58.27 kcal/mol, IP = 11.67 eV.

E. Photolysis. All photolyses were carried out on degassed (5 cycles) samples in quartz ESR tubes, using a Hanovia 450-W medium pressure mercury arc lamp with a Vycor 7910 filter sleeve (Ace Glass).

Photolysis of 1 in Cyclohexane-d_{12}. Photolysis of 9 mg of **1** in 0.5 mL of C_6D_{12} at room temperature for 8 h gave a product mixture (90% conversion) which was analyzed by ^1H NMR and GC. Bicyclo[1.1.0]butane (**16**) and cyclobutene (**17**) were observed and were identical with authentic samples in both ^1H NMR and t_R (both 1.2 min; 2.42 and 2.34 min respectively at 30 °C, linear velocity = 22 cm/s); yield of **16** ~70%; **17**, 1–2% (by NMR, GC). Remainder: ^1H NMR δ 2.3 (m, ~1 H), 5.0 (m, ~0.4 H), 5.7 (m, ~0.2 H); GC t_R, min (relative area) 2.5 (5), 9.1 (1), 12.8 (2). A

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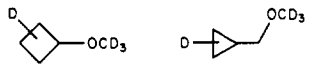
white precipitate was also observed.

Photolysis of 1 in Methanol-d_4. Photolysis of 12 mg of 1 in 0.5 mL of CD_3OD with ~5 mg of $NaHCO_3$ at room temperature produced a mixture which was analyzed by ^1H NMR and GC. Bicyclo[1.1.0]butane (16): yield (by NMR) 79% (1 h photolysis), 65% (3 h), 61% (5 h). Cyclobutene (17): yield ~2% (5 h). Methyl-d_3 4-pentenoate-2-d (14) (see section C): yield 16% (5 h). Cyclobutyl-d methyl-d_3 ether (24): ^1H NMR δ 1.5 (m, ~1 H), 1.7 (m, ~0.3 H), 1.85 (q, ~1.8 H), 2.2 (m, ~2 H), 3.85 (p, 1 H); yield ~6% (5 h). Cyclopropylcarbinyl-d methyl-d_3 ether (25): ^1H NMR δ 0.2 (m, 1.2 H), 0.5 (d, 1.9 H), 1.0 (sextet, 1 H), 3.2 (d, 2 H); yield ~6% (5 h). Retention times for 24 and 25 are 1.8 and 1.9 min but are unassigned. In the absence of $NaHCO_3$, no 16 was observed, and instead 24 and 25 were each obtained in 44% yield. In this case, the observed product distribution of 24-25 is identical with that reported by Wiberg and Szeimies[44] for the hydrolysis of bicyclobutane to the corresponding alcohols of 24-25. The observed labeling patterns are also nearly identical.



24 25

1,1-Di(methoxy-d_3)bicyclo[1.1.1]pentane (19) was formed in up to 43% yield from photolysis without $NaHCO_3$ at slightly below room temperature and was the sole observed product from photolysis at 35-40 °C. ^1H NMR δ 1.4 (s, 2 H), 2.0 (s, 2 H), 2.8 (s, 2 H); t_R 3.7 min.

Control Photolysis of 22. 1,3-Butadiene (~1 mg) in cyclohexane-d_{12} was photolyzed through Vycor for 8.5 h at room temperature. ^1H NMR and GC analysis showed that the yield of cyclobutene was less than 20% and that most of the starting material was unchanged.

Gas-Phase Photolysis of 1. Photolysis of 1-3 mg of 1 in an evacuated ESR tube with vacuum stopcock for durations up to 54 h at room temperature followed by vacuum transfer of benzene-d_6 into the tube, produced bicyclo[1.1.0]butane and 1,3-butadiene as products in a ratio which varied from experiment to experiment, with increasing pressure producing greater quantities of bicyclobutane. A colorless film was also formed on the sides of the tube (detected by filling the empty tube with 5% HF). Photolysis without the Vycor filter increased the rate, and the film on the sides of the tube was yellow instead of colorless.

Control Photolysis of 16. Bicyclo[1.1.0]butane (~6 mg) was photolyzed in the gas phase for 48 h at room temperature. Benzene-d_6 was vacuum transferred into the tube and the solution pipeted into an NMR tube. Only 16 was observed.

F. ESR Experiments. All samples were prepared and degassed (5 cycles) in 5-mm o.d. quartz ESR tubes equipped with high vacuum stopcocks. Samples typically contained 3-8 mg of 1 and 0.5 mL of solvent. 2-Methyltetrahydrofuran (MTHF), cyclohexane, benzene-d_6, and hexafluorobenzene were used as solvents. One sample was made in MTHF with a small amount of mercury as photosensitizer.

A Varian E-9 spectrometer and an Air Products and Chemicals Helitran liquid helium transfer apparatus were used.[58] The samples were photolyzed in the cavity by using an Oriel 200-W mercury-xenon lamp, operated between 150 and 180 W. The light was filtered with water in a quartz vessel.

The cavity temperature was measured using a calibrated chromel vs. gold (with 0.7% iron) thermocouple fitted inside a sample tube. The experiments were run in the temperature range from 9 to 12 K. Some samples exhibited doublet signals upon photolysis, but no signal which could be attributed to a triplet biradical was observed.

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Stereospecific Transformation of Grindelic Acid into the Antifeedant 6α-Hydroxygrindelic Acid, Its 6β-Epimer, and Other Related Natural Diterpene Acids

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The synthesis of the methyl esters of several natural diterpene acids related to grindelic acid (**1a**), including methyl 7α,8α-epoxygrindelate (**2a**), methyl 7α-hydroxy-8,17-didehydrogrindelate (**3a**), methyl 6,7,8,17-tetradehydrogrindelate (**4**), methyl 6-oxogrindelate (**6**), and methyl 6α-hydroxygrindelate (**7a**), through a common sequence is reported. The unusual, simultaneous, and stereospecific opening of the oxirane and tetrahydrofuran rings of the methyl 7α,8α-epoxygrindelate (**2a**) by aluminum isopropoxide to produce isopropyl 7α,9α-dihydroxylabda-8(17),13(*E*)-dien-15-oate (**8**) is also reported.

Some time ago as part of our research interest in transformations of natural products, we became aware of grindelic acid (**1a**), the most abundant diterpene acid from several *Grindelia* species.[1] Recently we decided to include 6-hydroxy derivatives of **1a** in a program designed to explore alternative methods of insect control.[2-4] Unfortunately our attempts to get the 6-hydroxy compounds through simple allylic oxidations of **1b** failed completely or led to useless complex mixtures. Apparently, oxidation occurs preferably on the allylic methyl group.[5]

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