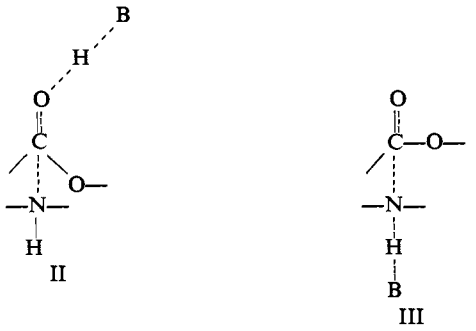
formation and decomposition of the tetrahedral intermediate are subject to such catalysis.

In view of the above considerations, a detailed analysis of all the existing data in terms of possible transition states for the general acid–base catalyzed reactions seems premature. However, it is possible that the apparent bifunctional catalysis by carboxylic acids (I) provides an important clue as to the correct transition states. If we assume, for the moment, that the monofunctional catalytic pathways partake of the individual aspects of the bifunctional transition state indicated in I, then we are led to the following transition states for general acid (II) and general base catalysis (III). Transition state III, which involves true general base catalysis, has previously been suggested by Jencks and Carriuolo[9] who have presented several arguments in its favor. Transition state II is similar to that proposed for general acid catalyzed attack of nucleophilic reagents on carbonyl substrates.[39,43–47] Concerning these transition states, two points are of interest. First, each of them is consistent with known data, much of which has been summarized above. Second, the failure to observe general acid catalysis for reactions involving tertiary amines (see the introductory section) does not provide a strong argument against transition state II, which might well occur with such amines, since such catalysis has never really been searched for with weakly basic tertiary amines whose conjugate acids, therefore, are reasonably strong acids and would be expected to be efficient catalysts.



II

III

Previous considerations regarding structure–reactivity relationships suggest that the value of ρ for reaction of a series of structurally related amines with substituted phenyl acetates might be a linear function of the pK_a of the nucleophilic reagent.[43,44,48] With this in mind, values of ρ for piperidine, morpholine, ethylenediamine, and glycine ethyl ester reactions with phenyl acetates were determined (Table IV). These values do not, in fact, vary in any systematic fashion with basicity of the nucleophilic reagent. Examination of these data in reference to more comprehensive collections (see ref 14 and 22) suggest that basicity *per se* is not the most important factor in the determination of ρ for these reactions.

(43) E. H. Cordes and W. P. Jencks, *J. Am. Chem. Soc.*, **84**, 4319 (1962).
(44) W. P. Jencks, *Progr. Phys. Org. Chem.*, **2**, 63 (1964).
(45) C. G. Swain and J. C. Worosz, *Tetrahedron Letters*, 3199 (1965).
(46) C. G. Swain, D. A. Kuhn, and R. L. Schowen, *J. Am. Chem. Soc.*, **87**, 1553 (1965).
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(48) S. I. Miller, *ibid.*, **81**, 101 (1959).

Solvolysis of Bicyclo[2.1.0]pentane-1-methyl *p*-Nitrobenzoate[1]

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Contribution from the Department of Chemistry, University of California, Berkeley, California 94720. *Received February 13, 1967*

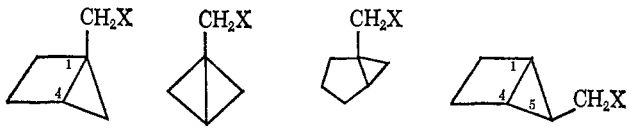
Abstract: Bicyclo[2.1.0]pentane-1-methanol (**1a**) was synthesized in a five-step reaction sequence from cyclobutanecarboxylic acid *via* 1-cyclobutenecarboxylic acid (**7**), the pyrazoline ester **8**, and the bicyclo[2.1.0]pentanecarboxylic acid ester **11**. The *p*-nitrobenzoate ester of **1a** was solvolyzed in 60% aqueous acetone at 50° to yield 3-methylenecyclopentanol (**12a**), and the rate of the reaction was 400,000 times faster than that of cyclopropylmethyl *p*-nitrobenzoate. Possible reasons for the large rate enhancement are discussed.

The remarkable facility of cyclopropane rings to stabilize carbonium ions has been demonstrated repeatedly. Cyclopropylcarbinyl cations are exceptionally stable, and the rates of reactions leading to them from cyclopropylcarbinyl, cyclobutyl, and allycarbinyl derivatives are greatly accelerated in comparison to related lesser strained, saturated systems. Considerable interest attends the nature of these rearrangements, and the structures of the intermediate carbonium ions have been the object of a large number of experimental studies and theoretical calculations.[3–5]

As part of a program to investigate the effects of conformation and strain on the reactivity of carbinyl derivatives attached to angular positions of a bicyclic fused ring system,[6] bicyclo[2.1.0]pentane-1-methanol (**1a**) has been prepared and the solvolytic rearrangement of its *p*-nitrobenzoate ester **1b** studied. The alcohol **1a** is a member of a homologous series, which in-

(1) This work was supported in part by Grant GP-3890, National Science Foundation.
(2) National Science Foundation Postdoctoral Fellow, 1964–1965.
(3) For recent reviews see: (a) N. C. Deno, *Progr. Phys. Org. Chem.*, 2, 129 (1964); (b) R. Breslow, "Molecular Rearrangements," Vol. 1, P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., Chapter 4; (c) M. J. S. Dewar and A. P. Marchand, *Ann. Rev. Phys. Chem.*, **16**, 321 (1965).
(4) For a thorough bibliography of recent work, see P. von R. Schleyer and G. W. Van Dine, *J. Am. Chem. Soc.*, **88**, 2321 (1966).
(5) (a) L. Birladeanu, T. Hanafusa, B. Johnson, and S. Winstein, *ibid.*, **88**, 3217 (1966); (b) M. Vogel and J. D. Roberts, *ibid.*, **88**, 2262 (1966).
(6) For the previous paper in this series, see W. G. Dauben and P. Laug, *Tetrahedron*, **20**, 1259 (1964).

cludes the alcohols **2a** and **3a**, whose solvolytic behavior has been previously investigated.[7,8] In addition, **1a** is structurally related to its positional isomer, bicyclo[2.1.0]pentane-5-methanol (**4a**), whose solvolytic behavior has been described by Wiberg and Ashe.[9] Al-



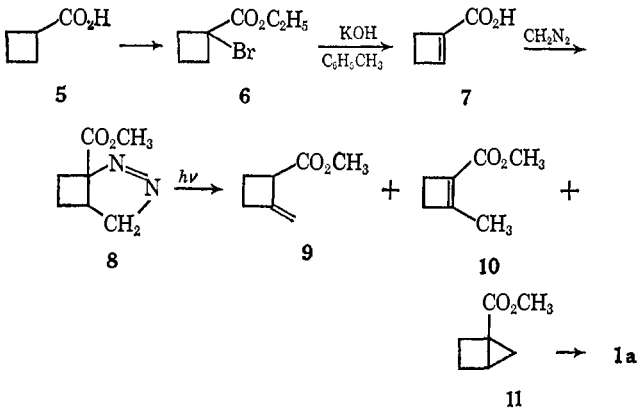
1a, X=OH **2a**, X=OH **3a**, X=OH **4a**, X=OH
b, X=OPNB **b**, X=OPNB **b**, X=OPNB **b**, X=OTs

though both **1a** and **4a** contain the same highly strained bicyclic system, it should be anticipated that their chemistry would differ markedly.

The number of rearrangement pathways open to the tosylate derivative **4b** is restricted by the position of attachment of the carbinyl group and the symmetry of the molecule. Heterolysis of the carbon–oxygen bond of **4b** can involve only the two equivalent carbon–carbon bonds (C_4–C_5 and C_1–C_5) of the cyclopropane ring. The strain of the molecule is not relieved during the ionization, but is increased. The rate of solvolysis of **4b** is slow, about the same as that of cyclopropylcarbinyl itself, and no rearrangement occurs during the reaction.

In contrast, ionization of **1b** can, in principle, involve participation of any of the three nonequivalent carbon–carbon bonds attached to the angular position. Involvement of the C_1–C_4 bond can result in the release of a considerable portion of the strain energy of the molecule, and it should be expected that the solvolysis of **1b** would lead to rearranged products at an accelerated rate.

Bicyclo[2.1.0]pentane-1-methanol was synthesized in a five-step reaction sequence starting with the commercially available cyclobutanecarboxylic acid (**5**). Bromination of the acid by the Hell–Volhard–Zelinsky method followed by work-up with ethanol led to the known ethyl 1-bromocyclobutane-1-carboxylate (**6**).[10] The bromo ester **6** was dehydrohalogenated with potassium hydroxide in boiling toluene, and the resulting cyclobutenecarboxylic acid (**7**) was treated immediately with an excess of diazomethane, yielding the pyrazoline ester **8**. The pyrazoline ester absorbs in the ultraviolet spectral region at 323 mμ (ε 192), and irradiation with

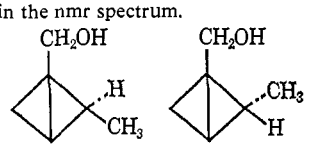


ultraviolet light caused the elimination of nitrogen and the formation of a mixture of the three esters **9**, **10**, and **11** in the ratio 2:3:7.5. The esters were separated by preparative vpc. The structure of the bicyclic ester **11** follows from its spectra.[10a] The ester **11** absorbs in the infrared region at 3060 cm^{-1} (cyclopropane C–H stretch) and at 1725 cm^{-1} (ester of a cyclopropanecarboxylic acid), and in the ultraviolet at 188 mμ (ε 7200). In the nmr spectrum of **11** only one of the cyclopropyl hydrogens is recognizable (quartet with J = 2 and 4 cps centered at τ 8.87), the others being obscured by complex absorption in the region τ 8.8–7.4. The methyl hydrogens appear as a singlet at τ 6.42. There was no absorption in the vinyl region. The structure of the α,β-unsaturated ester **10** likewise rests on spectral data (see Experimental Section). The minor component of the mixture was not collected in amounts sufficient for characterization, but its structure has been assigned tentatively as the β,γ-unsaturated ester **9** by analogy with the products formed in the decomposition of related pyrazoline esters[11] and on the basis of the following observations. The mixture of esters obtained by photolysis absorbs in the infrared at 890 cm^{-1}, whereas this region is transparent in the spectra of the two major products; the minor component was destroyed when the ester mixture was treated with the electrophilic reagents ozone or *m*-chloroperbenzoic acid.

Preparative vpc proved to be an inefficient method for the purification of **11** in amounts sufficient to complete the synthesis. Therefore, a chemical method of separation was sought, and ozonolysis proved to be the method of choice. Treatment of the mixture of esters with ozone destroyed the olefinic esters, and the bicyclic ester **11** was separated from the ozonides by filtration of the mixture through Super-Cel followed by chromatography on alumina. Reduction of the ester **11** with lithium aluminum hydride provided bicyclo[2.1.0]pentane-1-methanol (**1a**). The nmr spectrum of the alcohol **1a** shows two high-field protons at τ 9.30 and 9.37, five protons in the region τ 7.5 to 9.0, two protons in an AB quartet centered at τ 6.48 (J = 12 cps), and a singlet at τ 6.0 for the hydroxylic proton (disappears upon addition of deuterium oxide). The presence of the AB quartet at τ 6.48, assigned to the methylene bearing the hydroxyl group, shows that the methylene resides in an asymmetric environment; the lack of further splitting of the quartet indicates that the methylene is attached to a quaternary center. When this information is coupled with the empirical formula, $C_6H_{10}O$, required by the analytical data and the lack of unsaturation demanded by the infrared and nmr spectra, the structure of the alcohol **1a** is on firm ground.[12]

(7) K. B. Wiberg, G. M. Lampman, R. P. Ciula, D. S. Connor, P. Schertler, and J. Lavanish, *Tetrahedron*, **21**, 2749 (1965).
(8) W. D. Closson and G. T. Kwiatkowski, *ibid.*, **21**, 2779 (1965).
(9) K. B. Wiberg and A. J. Ashe, III, *Tetrahedron Letters*, 4245 (1965).
(10) A. Campbell and H. N. Rydon, *J. Chem. Soc.*, 3006 (1953).

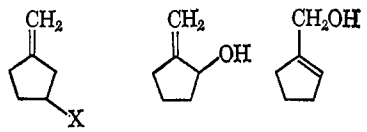
(10a) Note Added in Proof. This same synthetic sequence has just been supported by P. G. Gassman and K. T. Manfield, *J. Org. Chem.*, **32**, 915 (1967).
(11) T. V. van Auken and K. L. Rinehart, Jr., *J. Am. Chem. Soc.*, **84**, 3736 (1962).
(12) Structures i and ii, which might be expected to give an AB quartet for the methylene bearing the hydroxyl group, are not rationally possible from the synthetic sequence and are excluded by the lack of a doublet for the methyl group in the nmr spectrum.



i ii

Attempts to prepare the methanesulfonyl derivative of the alcohol **1a** were unsuccessful, leading to mixtures which contained chiefly 3-methylenecyclopentylmethanesulfonate and none of the desired bicyclic ester. Preparation of the less reactive *p*-nitrobenzoate **1b** by reaction of the alcohol **1a** with *p*-nitrobenzoyl chloride in pyridine, however, proceeded without difficulty. The crystalline ester **1b** was easily purified, and material of analytical purity was used in the solvolytic studies.

Sovolytic Studies. When a solution of the *p*-nitrobenzoate **1b** in 80% aqueous acetone was heated at 100° for 2 hr, there was obtained an 85% yield of *p*-nitrobenzoic acid and a neutral fraction which consisted of alcohols and *p*-nitrobenzoate esters. The alcohols were separated from the esters by bulb-to-bulb distillation. Vpc analysis of the alcohols, obtained in 60% yield, showed the presence of 3-methylenecyclopentanol (**12**; 91%), 2-methylenecyclopentanol (**13**; 5%), 1-hydroxymethylcyclopentene (**14**; 2%), and a fourth component of undetermined structure (2%). The allylic alcohols **13** and **14** were identified by comparison of their infrared and nmr spectra and vpc retention times with the authentic alcohols prepared by reduction



12a, X=OH **13** **14**
b, X=OPNB

of 2-ethoxycarbonylcyclopentanone with lithium aluminum hydride.[13] The structural assignment of 3-methylenecyclopentanol rests on its spectral and analytical data (see Experimental Section). When the mixture of alcohols was resubjected to solvolytic conditions (3 hr) in the presence of 1 equiv of *p*-nitrobenzoic acid, the relative amounts of the minor alcohols were increased at the expense of 3-methylenecyclopentanol (**12a**), indicating that at least the minor alcohols are formed in a secondary reaction. The nmr spectrum of the mixture of *p*-nitrobenzoates (obtained in 15% yield) showed it to be chiefly 3-methylenecyclopentyl *p*-nitrobenzoate (**12b**). None of the starting ester **1b** remained.

When the solvolysis was conducted in 60% aqueous acetone at 50° for 24 hr the composition of the alcohols obtained was **12a** (96%), **13** (3%), and **14** (trace). The *p*-nitrobenzoates obtained from the reaction in 19% yield were shown by nmr to consist of 3-methylenecyclopentyl *p*-nitrobenzoate (**12b**) and the bicyclic ester **1b**; reduction of the *p*-nitrobenzoates with lithium aluminum hydride produced the corresponding alcohols **1a** (78%) and **12a** (22%). Thus, the solvolysis under milder conditions is more selective and less of the rearranged returned *p*-nitrobenzoate **12b** is formed in the more aqueous solvent. In order to test the possibility that the alcohol **1a** is an intermediate in the solvolysis, the *p*-nitrobenzoate **1b** was solvolyzed at 50° in 60% aqueous acetone containing 2,6-lutidine to neutralize the *p*-nitrobenzoic acid formed in the reaction. The composition of the mixture of alcohols formed was essentially the same as when the solvolysis medium was unbuffered. Furthermore, the starting bicyclic alcohol **1a** was shown to be stable under the buffered solvolysis conditions. Thus, **1a** is not an intermediate in the solvolysis of **1b**. The *p*-nitrobenzoate **1b** was also subjected to solvolysis in acetic acid, and results were essentially the same as those reported above in 80% aqueous acetone, with the exception that acetates were produced rather than alcohols.

The rate of solvolysis of **1b** was determined in 60% aqueous acetone by titration of the *p*-nitrobenzoic acid formed in the reaction. The rate constants for the reaction at two temperatures are given in Table I along with the rate constants for **2b** and **3b**. Also included for comparison is the estimated relative rate of the same ester of the isomeric **4a**.

Table I. Rate Constants for Solvolysis of Alkyl *p*-Nitrobenzoates

p-Nitrobenzoate	Rate constants × 10^5, sec^{-1} in 60% aqueous acetone 50°	70°	100°	Relative rate
Cyclopropylmethyl			0.003[a]	1
Bicyclo[3.1.0]hexane-1-methyl			2.17[a]	725
Bicyclo[2.1.0]pentane-1-methyl	4.7	52.5	1200[b]	400,000
Bicyclo[1.1.0]butane-1-methyl				>1,000[c]
Bicyclo[2.1.0]pentane-5-methyl				1.3[d]

[a] Reference 8. [b] Calculated from values at 50 and 70°. [c] Comparison with cyclopropylmethyl *p*-nitrobenzoate in 90% aqueous acetone at 118.6°.[7] [d] Comparison of tosylate esters in acetic acid.[9]

The order of reactivity shown in Table I reflects the availability of strain energy of the various systems for the assistance of ionization. Bicyclopentane has a strain energy of 53.6 kcal/mole,[14] and cyclopentane a strain energy of 6.5 kcal/mole. Thus, a reaction involving conversion of a bicyclo[2.1.0]pentane to a cyclopentane would release a maximum of 47 kcal/mole, a portion of which could be available in attaining the transition state. Similarly, a reaction involving the conversion of a bicyclobutane (strain energy 64 kcal/mole[4]) to a cyclobutane (strain energy 26 kcal/mole[15]) releases a maximum of 38 kcal/mole. Although bicyclo[2.1.0]pentane-1-methyl *p*-nitrobenzoate has less strain energy than bicyclo[1.1.0]butane-1-methyl *p*-nitrobenzoate, more of its strain energy is available to assist in the ionization step. Consequently, the bicyclopentane derivative **1b** solvolyzes at a rate which is higher than that of the two adjacent members of the homologous series. It is noteworthy that **1a** is the most reactive primary cyclopropylcarbinol yet investigated. Furthermore, it is of interest to note the large difference in rate between the 1- and 5-carbinyl derivatives of the bicyclo[2.1.0]pentyl system. With this latter isomer, simple bond migration will not lead to a large diminution of strain in the ring system, indicative of the importance of this feature of the reaction.

Participation of the cyclopropane ring in **1b** during the cleavage of the alkyl oxygen bond provides a mechanism whereby the strain energy of the bicyclo[2.1.0]pentane system may be utilized in attaining the transition state.

(13) A. S. Dreiding and J. A. Hartman, *J. Am. Chem. Soc.*, 75, 939 (1953).

(14) R. B. Turner, "Kekule Symposium," Butterworths Scientific Publications, London, 1959, p 67.

(15) (a) S. Kaarsemaker and J. Coops, *Rec. Trav. Chim.*, 71, 261 (1952); (b) Y. I. Gol'dfarb and L. I. Belen'kii, *Usp. Khim.*, 214 (1960).

Ionization of **1b** probably leads to the strained cyclopropylcarbinyl cation **15**. Due to the strain of the cation **15**, the 1,4 bond is longer than the 1,5 bond, and

15

the electrons of the 1,4 bond are delocalized to a greater degree than those of the 1,5 bond. The lengthening of the 1,4 bond accounts for the relief of strain in proceeding to the transition state, and the greater degree of delocalization of the electrons of the 1,4 bond causes a greater portion of the positive charge to be localized on carbon atom 4. Attack of the solvent on carbon 4 of cation **15** leads to alcohol **12a** and attack of *p*-nitrobenzoate anion leads to rearranged returned *p*-nitrobenzoate **12b**. Formation of the classical 3-methylenecyclopentyl cation as an additional intermediate in the reaction cannot be ruled out on the basis of the data presently available. In comparison, in the 5-carbinyl derivative **4** which is the slowest reacting member of this series, the placement of the carbinyl group at C-5 does not allow for participation of the 1,4 bond in the transition state. Such bond lengthening is the most important feature needed to greatly reduce the strain of the system.

Experimental Section[16]

1-Methoxycarbonyl-2,3-diazabicyclo[3.2.0]hept-2-ene (8). To a stirred refluxing mixture of 20.0 g of 85% potassium hydroxide and 250 ml of toluene contained in a 500-ml, three-necked flask equipped with a reflux condenser, dropping funnel, and nitrogen inlet was added 19.05 g (0.092 mole) of ethyl 1-bromocyclobutanecarboxylate.[10] The rate of addition was adjusted to maintain the temperature at the boiling point without further heating. After the addition was complete (45 min), the heat was again applied, and the mixture was refluxed for an additional hour. The cooled reaction mixture was transferred to a separatory funnel with the aid of 100 ml of water. The aqueous layer was separated, washed with pentane, acidified with dilute hydrochloric acid, and extracted with several portions of ether. The combined ether extracts were washed once with water and once with saturated sodium chloride solution, dried over anhydrous sodium sulfate, and filtered.

An ethereal solution of diazomethane, prepared from 35 g of N-nitroso-N-methylurea, was added to the filtrate, and the resulting solution was placed in the refrigerator for 4 days. The excess diazomethane was destroyed by the dropwise addition of acetic acid, and the solution was washed twice with saturated sodium bicarbonate solution, once with water, and once with saturated sodium chloride solution, dried over anhydrous sodium sulfate, and filtered. The solvent was removed and the residual oil distilled at reduced pressure. The pyrazoline ester **8** (11.66 g, 85%) distilled at 63–68° (0.3–0.7 mm); $\nu_{max}^{CCl_4}$ 1745, 1540, 1430 cm^{-1}; λ_{max}^{EtOH} 323 mμ (ε 192); nmr (τ, CCl_4) 5.41 (singlet, 1 H), 5.47 (doublet, J = 2 cps, 1 H), 6.30 (singlet, 3 H), 7.0–8.2 (complex, 4 H), 8.4–9.0 (complex, 1 H).

Anal. Calcd for $C_7H_{10}N_2O_2$: C, 54.56; H, 6.54; N, 18.17. Found: C, 54.72; H, 6.77; N, 18.28.

Photolysis of 1-Methoxycarbonyl-2,3-diazabicyclo[3.2.0]hept-2-ene (8). A solution of 10.56 g (0.0685 mole) of 1-methoxycarbonyl-2,3-diazabicyclo[3.2.0]hept-2-ene in 2 l. of ether was irradiated through a Pyrex filter for 11 hr with light from a Hanovia 450-w lamp (type L, no. 679A-36). During the irradiation the ultraviolet absorption at 326 mμ (λ_{max} in pentane) gradually decreased to zero. The solvent was removed by distillation and the residual yellow oil (9.45 g) was dissolved in pentane and passed through a column of neutral alumina III. Pentane (350 ml) eluted a clear colorless oil (9.3 g). Analysis of the oil by vpc (5 ft × 0.25 in column of DEGS on Chromosorb W, 94°, 60 cc of He/min) showed 13% pentane and three compounds with retention times of 5.4, 6.9, and 8.2 min in the ratio 2:3:7.5. The latter two compounds were separated by preparative vpc. The compound with retention time 6.9 min was assigned structure **10**; $\nu_{max}^{CCl_4}$ 1720, 1665 cm^{-1}; λ_{max}^{EtOH} 227 mμ (ε 12,400); nmr (τ, CCl_4) 6.37 (singlet, 3 H), 7.35–7.80 (complex, 4 H), 8.01 (broad singlet, 3 H). The compound with retention time 8.2 min was assigned structure **11**; $\nu_{max}^{CCl_4}$ 3070, 1735 cm^{-1}; λ_{max}^{EtOH} 188 mμ (ε 7200); nmr (τ, CCl_4) 6.44 (singlet, 3 H), 7.3–8.10 (complex, 3 H), 8.2–8.75 (complex, 3 H), 8.87 (quartet, 1 H, J = 2 and 4 cps).

Anal. Calcd for $C_7H_{10}O$: C, 66.65; H, 7.99. Found: C, 66.38; H, 7.87.

Ozonolysis of Mixture of Esters from Photolysis. A solution of 6.46 g (0.512 mole) of the mixture of esters obtained from the photolysis was dissolved in 30 ml of pentane and cooled to −78°. Ozone was passed through the solution at the rate of 0.7 mmole/min for 35 min, at which time the solution ceased to absorb ozone. The ozonides of the olefinic esters precipitated as an oil which was removed by filtration of the cold solution through Super-Cel. The filtrate was passed through a column of 80 g of neutral alumina III, followed by an additional 300 ml of pentane. The main portion of pentane was removed by distillation through a 20-cm Vigreux column and the last portion was removed on the water aspirator. The residual clear colorless liquid (2.06 g, 32%) was shown by its infrared and nmr spectra and the vpc retention time to be the bicyclic ester **11**, completely free of the two isomeric esters **9** and **10**.

Bicyclo[2.1.0]pentane-1-methanol (1a). 1-Methoxycarbonylbicyclo[2.1.0]pentane (1.78 g, 0.014 mole) was added slowly to a stirred solution of 0.631 g (0.0166 mole) of lithium aluminum hydride in 50 ml of ether at 0°. The mixture was stirred for 3.0 hr at 0°, water was added, and the resulting suspension was filtered through Super-Cel with the aid of additional ether. The solution was dried over anhydrous sodium sulfate and filtered. The solvent was removed by distillation first at atmospheric pressure through a 20-cm Vigreux column and finally at water aspirator vacuum using a rotary evaporator. The residual liquid (1.10 g, 80%) showed a single peak on analysis by vpc (20% Carbowax 20M on Firebrick with 10% KOH, 98°, 60 cc of He/min); $\nu_{max}^{CCl_4}$ 3600, 3300–3400, 3060, 1025 cm^{-1}; nmr (τ CCl_4) 6.0 (singlet, 1 H), 6.47 (AB quartet, 2 H, J = 12 cps), 7.6–8.9 (complex, 5 H), 9.31 and 9.36 (two singlets, 2 H). An analytical sample was prepared by preparative vpc.

Anal. Calcd for $C_6H_{10}O$: C, 73.43; H, 10.27. Found: C, 73.68; H, 10.49.

Bicyclo[2.1.0]pentane-1-methyl *p*-Nitrobenzoate (1b). A solution of *p*-nitrobenzoyl chloride (4.00 g, 0.026 mole) in 40 ml of dry pyridine was cooled in an ice bath. To the cooled solution was added a solution of 1.80 g (0.0184 mole) of bicyclo[2.1.0]pentane-1-methanol (**1a**) in 10 ml of pyridine. The mixture was stirred for 1.5 hr, then poured into water and extracted with several portions of petroleum ether. The combined petroleum ether extracts were washed successively with saturated sodium bicarbonate solution and water, dried over anhydrous sodium sulfate, and filtered. The solvent was removed under high vacuum overnight. The oily residue (4.3 g, 95%), which was nearly pure by its nmr spectrum, was crystallized and recrystallized from petroleum ether, giving 3.19 g (70%) of bicyclo[2.1.0]pentane-1-methyl *p*-nitrobenzoate (**1b**); mp 40–42°; $\nu_{max}^{CCl_4}$ 3060, 1725, 1605, 1270 cm^{-1}; nmr (τ, CCl_4) 1.81 (singlet, 4 H, aromatic), 5.62 (singlet, 2 H, carbinyl methylene), 7.65–9.03 (complex, 5 H), 9.10 and 9.17 (two broadened singlets, 2 H, cyclopropyl).

Anal. Calcd for $C_{13}H_{13}NO_4$: C, 63.15; H, 5.30; N, 5.66. Found: C, 62.99; H, 5.19; N, 5.58.

Sovolysis of Bicyclo[2.1.0]pentane-1-methyl *p*-Nitrobenzoate (1b). A solution of 1.002 g (4.05 mmoles) of bicyclo[2.1.0]pentane-1-methyl *p*-nitrobenzoate in 30 ml of 80% aqueous acetone (prepared by mixing one volume of water with four volumes of acetone) was sealed in a glass ampoule and placed in a bath of boiling water. After 2 hr the ampoule was opened and the contents were poured into 50 ml of saturated sodium bicarbonate solution. The solution was extracted with several portions of ether and the combined ether extracts were washed with water, dried over sodium sulfate, and filtered. The volume of the solution was reduced to 5 ml by distillation at atmospheric pressure and the remaining solvent was removed on a rotary evaporator to give an oily residue (385 mg). The residue was separated into a volatile fraction and a nonvolatile fraction by distillation at 70° (0.1–2 mm) into a receiver cooled to −78°. The aqueous solution remaining after the ether extraction was acidified and extracted with ether. The combined extracts were washed with water, dried over anhydrous sodium sulfate, filtered, and evaporated to dryness on a rotary evaporator to give 572 mg (84%) of *p*-nitrobenzoic acid.

(16) Combustion analyses were performed by the Microanalytical Laboratory, College of Chemistry, University of California, Berkeley, Calif.

The volatile fraction (238 mg) was analyzed by vpc (20% DEGS on Chromosorb W, 5 ft × 0.25 in column, 101°, 60 cc of He/min) giving the following peaks: A, 4.6 min (5%); B, 5.1 min (2%); C, 6.5 min (91%); and D, 8.5 min (2%).

Component C, 3-methylenecyclopentanol (**12**), was obtained pure by preparative vpc under the conditions described above: $\nu_{max}^{CCl_4}$ 3600, 3400 (broad), 3070, 2960, 1655, 1063, 1020, 880 cm^{-1}; nmr (τ, CCl_4) 5.18 (pentuplet, J = 2 cps, 2 H, exocyclic methylene), 5.75 (pentuplet, J = 4.5 cps, 1 H, methine), 7.07 (singlet, 1 H, hydroxyl), 7.50–7.85 (complex, 4 H, allylic methylenes), 7.90–8.50 (complex, 2 H, nonallylic methylene).

Anal. Calcd for $C_6H_{10}O$: C, 73.43; H, 10.27. Found: C, 73.24; H, 10.12.

Component D was also obtained pure, and its infrared and nmr spectra and vpc retention time were identical with those of authentic cyclopentene-1-methanol (**14**) prepared by lithium aluminum hydride reduction of 2-ethoxycarbonylcyclopentanone.[13] The spectral properties of **14** are: $\nu_{max}^{CCl_4}$ 3600, 3400 (broad), 3020, 2940, 1655, 1430, 1040 cm^{-1}; nmr (τ, CCl_4) 4.48 (complex, 1 H, vinyl), 5.96 (slightly broadened singlet, 2 H, carbinyl methylene), 6.20 (singlet, 1 H, hydroxyl), 7.45–7.85 (complex, 4 H, allylic methylenes), 7.90–8.30 (complex, 2 H, nonallylic methylene).

Components A and B could not be obtained free from one another, but A could be identified as 2-methylenecyclopentanol (**13**). The vpc retention time of component A was identical with that of authentic **13**, prepared by lithium aluminum hydride reduction of 2-ethoxycarbonylcyclopentanone,[13] and the infrared and nmr spectra of the mixture of components A and B showed all the absorption bands present in the spectra of pure authentic **13**. For the authentic alcohol **13** the spectral properties are: $\nu_{max}^{CCl_4}$ 3600, 3400 (broad), 3060, 2930, 1800, 1655, 1420, 898 cm^{-1}; nmr (τ, CCl_4) 4.98 and 5.12 (two broadened singlets, 1 H each, exocyclic methylene), 5.73 (broad hump, 1 H, methine), 6.34 (singlet, 1 H, hydroxyl), 7.45–7.85 (complex, 2 H, allylic methylene), 7.95–8.70 (complex, 4 H, nonallylic methylene). Component B was not identified.

The nonvolatile fraction (147 mg) was a mixture of *p*-nitrobenzoate esters; $\nu_{max}^{CCl_4}$ 1725, 1265, 720 cm^{-1}. Integration of the nmr spectral areas for the aromatic protons (τ 1.85) and the vinyl proton bands (τ 4.95–5.30) indicated the mixture was 60% 3-methylenecyclopentyl *p*-nitrobenzoate (**12b**). There was no absorption at τ 9.1–9.2, showing that the starting ester **1b** was not present.

Isomerization of the Mixture of Alcohols from the Solvolysis. A portion (60 mg) of the mixture of alcohols obtained from the solvolysis was dissolved in 5 ml of 80% aqueous acetone containing 125 mg of *p*-nitrobenzoic acid. The solution was sealed in a glass ampoule and heated to 100° for 3 hr. The ampoule was cooled and opened, and the alcohols were reisolated as described in the hydrolysis experiment. Analysis of the recovered alcohols (30 mg) by vpc showed the mixture to have the following composition: **13** (component A, 10%), unknown (component B, 5%), **12a** (component C, 83%), and **14** (component D, 2%).

Solvolysis of Bicyclo[2.1.0]pentane-1-methyl *p*-Nitrobenzoate (1b) in 60% Aqueous Acetone. In an experiment similar to that described above for the hydrolysis in 80% aqueous acetone, **1b** was hydrolyzed in 60% aqueous acetone at 50° for 16 hr. The mixture of alcohols obtained consisted of **13** (3%), unknown (1%), **12a** (96%), and **14** (trace).

The nonvolatile fraction of *p*-nitrobenzoates (obtained in 19% yield) was shown to be a 3:1 mixture of the starting ester **1b** and 3-methylenecyclopentyl *p*-nitrobenzoate (**12b**) by integration of the appropriate areas of the nmr spectrum. The mixture of *p*-nitrobenzoates was reduced with lithium aluminum hydride to the corresponding alcohols. The mixture of alcohols was analyzed by vpc and had the following compositions: **1a** (78%) and **12a** (22%).

Solvolysis of Bicyclo[2.1.0]pentane-1-methyl *p*-Nitrobenzoate (1b) under Buffered Conditions. 2,6-Lutidine (146 mg, 1.36 mmoles) and the *p*-nitrobenzoate **1b** (271 mg, 1.10 mmoles) were dissolved in 60% aqueous acetone, and the solution was warmed to 50° for 24 hr. The mixture was poured into water and extracted with pentane. The pentane solution was washed with saturated sodium chloride solution, dried over sodium sulfate, filtered, and distilled at atmospheric pressure until *ca.* 0.5 ml remained. Analysis of the residue by vpc showed it contained the alcohols **13** and **12a** in a ratio of 3:97. None of the starting bicyclic alcohol **1a** could be detected.

Stability of Bicyclo[2.1.0]pentane-1-methanol (1a) under Buffered Solvolysis Conditions. The bicyclic alcohol **1a** (30 mg, 0.3 mmole) was added to 10 ml of 60% aqueous acetone containing 40 mg (0.24 mmole) of *p*-nitrobenzoic acid and 108 mg (1 mmole) of 2,6-lutidine. The solution was placed in a bath at 50° for 24 hr and the alcohol was reisolated as described in the above experiment. Analysis of the recovered alcohol by vpc showed it was unchanged; none of the isomeric alcohols could be detected.

Kinetic Experiments. Aqueous acetone, 60%, was prepared by mixing three volumes of acetone (distilled from potassium permanganate) with two volumes of distilled water at 25°. The solvolysis rate at 70° was determined by the ampoule technique, and the solvolysis rate at 50° was determined by withdrawing aliquots from a volumetric flask. The aliquots were titrated with 0.0208 *N* sodium hydroxide solution using brom thymol blue indicator. Rates at both temperatures were run in duplicate. The first-order rate constants drifted with time due to internal return, and the values are reported for the first half-life.