fluence on the stability of the *exo* substituent. However, both of these possibilities must either be minor contributors to the stability of the substituted bicyclo[2.2.2]octenes or to a large degree cancel each other. Other examples will have to be examined to provide additional support for the proposed stability controlling features in the bicyclo[2.2.2]octenes.

Only one additional equilibration in the bicyclo[2.2.2]octenes has been examined. LeBel[7] observed that the *endo*-bicyclo[2.2.2]oct-2-en-5-ol is more stable than the *exo* isomer in the presence of aluminum isopropoxide in isopropyl alcohol containing a few drops of acetone. The difference in energy is 0.40 kcal/mole. Our method of analysis using 0.75 kcal/mole as the conformational preference of the hydroxyl group predicts that the *endo* isomer would be more stable by 0.38 kcal/mole. It is disturbing, however, to note that by using aluminum *t*-butoxide in benzene containing a trace of fluorenone LeBel obtained a 59:41 ratio of *exo* to *endo* alcohol.

Experimental Section

2-Cyanobicyclo[2.2.2]oct-5-ene.—2-Cyanobicyclo[2.2.2]oct-5-ene was prepared according to the method of Alder.[8] The isomeric nitriles were separated by vapor phase chromatography on a 20% QF-1 on Chromosorb W column. The *endo* isomer, which predominated in the reaction mixture, had the longer time. The *exo* and *endo* isomers melted at 52–53° (lit.[8] 53°) and 66–67° (lit.[8] 66°), respectively. Hydrogenation of either isomers in ethanol with platinum oxide catalyst yielded the known 2-cyano bicyclo[2.2.2]octane, mp 129° (lit.[8] 128°).

5-Acetylbicyclo[2.2.2]oct-2-ene.—The Diels–Alder reaction between 1,3-cyclohexadiene and methyl vinyl ketone was carried out as described for the preparation of 5-acetylbicyclo[2.2.2]hept-2-ene.[9] Fractional distillation of the reaction mixture afforded a mixture of the *exo* and *endo* adducts, bp 62° (2 mm). A portion of the mixture was separated by vapor phase chromatography on a 20% QF-1 on Chromosorb W column. The major product had the longer retention time and was assigned as the *endo* isomer in accord with the known course of the Diels–Alder reaction and the behavior of similar compounds on the column employed.

Equilibrium Determinations.—The analytical procedure for the determination of the equilibrium constants listed in Table I have been described in an earlier paper of this series.[3]

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[7] N. A. LeBel and J. E. Huber, *J. Am. Chem. Soc.*, **85**, 3193 (1963).

[8] K. Alder, K. Heimbach, and R. Reubke, *Chem. Ber.*, **91**, 1516 (1958).

[9] J. G. Dinwiddle, Jr., and S. P. McManus, *J. Org. Chem.*, **30**, 766 (1965).

Lead Tetraacetate. III. Reactions with 5-Hexen-1-ol, Cyclohexenols, and Cyclooctenols[1]

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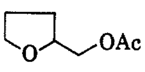
The formation of acetoxy cyclic ethers from the reaction of lead tetraacetate with olefinic alcohols has been reported in aliphatic,[2] bicyclic,[3] and steroidal[4] systems. In an aliphatic system, the position of the double bond plays an important role in determining the course of reaction. Thus, allyl acetate resulted from the reaction of 3-buten-1-ol, whereas 4-penten-1-ol yielded the cyclization products **1** and **2**.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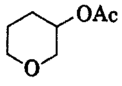
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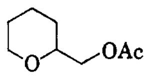
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To investigate the scope of this cyclization reaction, the study was extended to a longer chain aliphatic olefinic alcohol and some cyclic six- and eight-membered olefinic alcohols.

As shown in Table I, different solvents produce marked changes in the product distribution. The highest yield of the cyclic ether **3** was obtained in benzene; none was found from pyridine. One notes that in pyridine an aldehyde was obtained in fair yield, a result supporting previous reports[5,6] that primary alcohols are oxidized to aldehydes with lead tetraacetate in pyridine in good yields.

TABLE I
PRODUCTS OF REACTION OF LEAD TETRAACETATE WITH 5-HEXEN-1-OL

Product	Yield[a] Benzene[b]	Yield[a] Cyclohexane[b]	Yield[a] Pyridine[c]
5-Hexen-1-yl acetate	12	21	20
5-Hexenal	0	0	19
5-Hexen-1-ol	3	3	9
2-Acetoxymethyltetrahydropyran (**3**)	37	21	0
Unknowns	21	20	
Total yield	73	65	48

[a] Per cent yields, based on the starting alcohol, were determined by gas chromatographic analysis corrected by the use of a standard. [b] At reflux, 12 hr. [c] Room temperature, 12 hr.

In order to show whether a cyclic ether would be formed from cyclohexenols, the products of reaction with lead tetraacetate were investigated.

Table II shows that the oxidation product, 2-cyclohexen-1-one, was the major product from 2-cyclohexen-1-ol, whereas none of the ketone was obtained from 3-cyclohexen-1-ol. It is clear that the presence of a double bond in the allylic position facilitates oxidation. However, the presence of a double bond must not be a requirement for the oxidation reaction since cyclohexanol itself was also oxidized to cyclohexanone under the reaction conditions. No acetoxy ethers were found in the products from cyclohexenols; their absence may be due to the strain expected in the bicyclic system of these compounds. Another factor may be that the geometry of the molecule is such that the hydroxyl group is not close enough to the double bond for a favorable interaction.

Cyclohexanetriol triacetates, products expected from the addition of lead tetraacetate to the double bond, were not found in either case. An isolated double bond, for example, cyclohexene,[7] reacts with lead tetraacetate

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[1] Paper II: S. Moon, *J. Org. Chem.*, **29**, 3456 (1964).

[2] S. Moon and J. M. Lodge, *ibid.*, **29**, 3453 (1964).

[3] R. M. Moriarity and K. Kapadia, *Tetrahedron Letters*, 1165 (1964).

[4] H. Immer, M. Lj. Mihailovic, K. Schaffner, D. Arigoni, and O. Jeger, *Helv. Chim. Acta*, **45**, 753 (1962).

[5] R. E. Partch, *Tetrahedron Letters*, 3071 (1964).

[6] M. Lj. Mihailovic, Z. Cekovic, Z. Maksimovic, D. Jeremic, Lj. Lorenc, and R. I. Mamuzic, *Tetrahedron*, **21**, 2799 (1965).

[7] C. B. Anderson and S. Winstein, *J. Org. Chem.*, **28**, 605 (1963).

TABLE II

PRODUCTS OF REACTION OF LEAD TETRAACETATE WITH CYCLOHEXENOLS

	2-Cyclo-hexen-1-ol	3-Cyclo-hexen-1-ol	Cyclohexanol
Alcohol/LTA (g/g)	1.2/2	1/4	2/4
Benzene, ml	25	20	20
Time of reflux, hr	12	12	12
Gc data	Column B, 135°	Column A, 185° Column B, 155° Column D, 125°	Column D, 127°
Products, (%)			
ketone	58	0	5
acetate	16	80	28
alcohol	1	10	25
total yield	75	90	58

readily. We found that the reaction of cyclohexene was complete after 3 hr in acetic acid at 80°. 2-Cyclohexen-1-yl acetate, on the other hand, was recovered unchanged after treatment with lead tetraacetate in acetic acid at 80° for 3 hr. The unreactivity of the double bond in the allylic acetate may be due to an inductive effect of the acetoxy group. Peterson[8] reported that the acetoxy group as a substituent retards electrophilic addition to olefins.

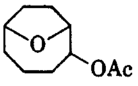
TABLE III

PRODUCTS OF REACTION OF LEAD TETRAACETATE WITH CYCLOOCTENOLS

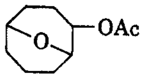
	Products[a]				
Alcohol	Ketone	Acetate	Alcohol	Acetoxy ether	Total yield
2-Cycloocten-1-ol					
in benzene[b]	2	61	11		74
in cyclohexane[b]	2	18	31		51
in pyridine[c]	20	13	11		44
3-Cycloocten-1-ol					
in cyclohexane[b]	0	65	7		72
in pyridine[c]	41	4	0		45
4-Cycloocten-1-ol					
in benzene[b]	5	5	0	70	80
in cyclohexane[b]	5	17	0	36	58
in pyridine[c]	52	4	0	0	56

[a] Percentage yields, based on the starting alcohol, were determined by gas chromatographic analysis corrected by the use of a standard. [b] At reflux, 12 hr. [c] At room temperature, 12 hr.

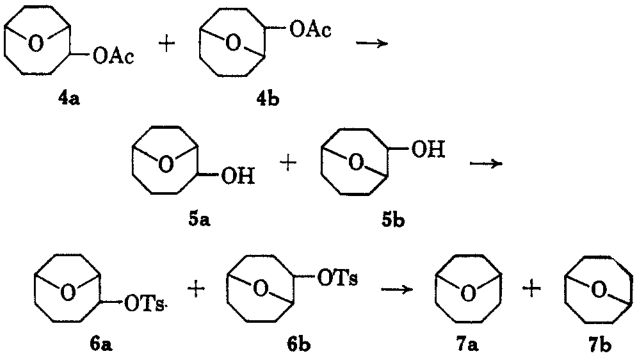
4-Cycloocten-1-ol on treatment with lead tetraacetate in boiling benzene produced as major products compounds to which the structures **4a** and **4b** were assigned.[9] These compounds could not be separated by gas chromatography. In support of the assignment, the infrared spectrum of the mixture showed no unsaturation but indicated the presence of an acetoxy group. The nmr spectrum is consistent with the assignment. It shows absorptions at τ 4.95 (multiplet, the proton α to the acetoxy group), 5.50, 6.04 (multiplets, the protons on the epoxy carbons), and 7.93, 7.96 (singlets, the acetoxy methyl groups). Further support of the structural assignment was obtained when the mixture of acetoxy ethers **4a** and **4b** was converted to the known[10] ethers, **7a** and **7b**, separable by gas chromatography. The acetoxy ethers **4a** and **4b** were converted to the corresponding alcohols **5a** and **5b** with lithium aluminum hydride, and then to the tosylates **6a** and **6b**. The toslyates were treated with lithium aluminum hydride to give the ethers **7a** and **7b** in a relative ratio of 40 to 60, indicating that the ratio of the acetoxy ethers **4a** and **4b** was 40 to 60.



4a



4b



The corresponding acetate and the unchanged alcohol were minor products from 4-cycloocten-1-ol. It is noteworthy that the yield of the acetate was small, whereas normally a high yield of an acetate is obtained from an alcohol.

2- and 3-cycloocten-1-ol gave the corresponding acetate as a major product when benzene or cyclohexane was used as a solvent. Very little or no ketone was formed from the alcohols. When pyridine was used as solvent, the corresponding ketones were obtained in high yield from 2-, 3-, and 4-cycloocten-1-ol. That there was no migration of the double bond during the oxidation was shown when the ketones, isolated and reduced with lithium aluminum hydride, gave the corresponding alcohols not contaminated by the isomeric alcohols.

Experimental Section[11]

Reactions of 5-Hexen-1-ol with Lead Tetraacetate. (a) In Benzene.—A mixture of 1 g of 5-hexen-1-ol, 4 g of lead tetraacetate, and 20 ml of benzene was heated under reflux overnight. The mixture was cooled to room temperature and stirred with 5 ml of ethylene glycol for 15 min in order to decompose any excess lead tetraacetate. The benzene layer was separated, washed with water, 10% potassium iodide solution, 10% sodium bicarbonate solution, and water, and dried (magnesium sulfate). The benzene was removed by distillation. Gas chromatographic analysis of the product showed that there were four components.

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[8] P. E. Peterson and G. Allen, *J. Am. Chem. Soc.*, **85**, 3608 (1963).

[9] We learned from Professor A. C. Cope that his group obtained the same compounds from 4-cycloocten-1-ol on treatment with LTA. We are indebted to Professor Cope for making his results available to us prior to publication.

[10] A. C. Cope and B. C. Anderson, *J. Am. Chem. Soc.*, **79**, 3892 (1957); A. C. Cope and A. Fournier, Jr., *ibid.*, **79**, 3896 (1957).

[11] For gas chromatographic analyses, an F and M Model 810 flame ionization gas chromatograph and gas chromatograph with thermal conductivity detectors were used. The liquid phase absorbants employed were Dow-Corning silicone oil No. 710 (column A), silicone rubber (SE-30) (column B), 1,2,3-tris-(cyanoethoxy)propane (TCEP) (column C), Carbowax 1540 (column D), and ethylene glycol adipate (column E). Infrared spectra were recorded with Perkin-Elmer Infrarcord Model 337, nmr spectra with a Varian A-60 nmr spectrometer.

The first three were identified as 5-hexen-1-ol (3%),[12] 5-hexen-1-yl acetate (12%), and 2-acetoxymethyltetrahydropyran (37%), by comparison[13] with authentic samples. The component of longest retention time (21% yield) was not identified. Its infrared spectrum indicated unsaturation but showed no band in the carbonyl region.

(b) **In Cyclohexane.**—A mixture of 2 g of 5-hexen-1-ol, 8.86 g of lead tetraacetate, and 100 ml of cyclohexane was heated to reflux overnight. It was cooled to room temperature and the products were isolated as described for the reaction in benzene.

(c) **In Pyridine.**—A mixture of 2 g of 5-hexen-1-ol, 8.86 g of lead tetraacetate, and 100 ml of dry pyridine was sitrred at room temperature overnight. The solution was diluted with 100 ml of water and extracted with three 100-ml portions of ether. The ether extracts were combined and washed with 6 *N* hydrochloric acid, water, 10% sodium bicarbonate, water and brine, and dried over magnesium sulfate. Gas chromatography (column B, 135°) revealed three components which were identified as 5-hexen-1-ol,[13] 5-hexen-1-yl acetate,[13] and 5-hexenal (λ_{max} 3080, 2930, 2810, 2710, 1730, 995, 915, 730 and 695 cm^{-1}; nmr (CCl_4) τ 0.27 (triplet, 1 H), 4.30, 4.90, 5.10 (multiplets, 3 H), and 7.8 (multiplets 6 H).

Reaction of 4-Cycloocten-1-ol with Lead Tetraacetate.—A mixture of 5.0 g of 4-cycloocten-1-ol, 20.0 g of lead tetraacetate, and 200 ml of dry benzene was heated under reflux with stirring for 12 hr. It was cooled to room temperature, 5 ml of ethylene glycol was added, and the mixture was stirred at room temperature for 30 min. The organic layer was separated and washed successively with water, 20% potassium iodide, water, and brine. The benzene solution was dried over magnesium sulfate and concentrated by distillation. The product was distilled through a spinning-band column, giving 1.97 g, bp 75–76 (0.7 mm). The distillate contained, in addition to the alcohol and the acetate, a mixture of two isomeric acetoxy ethers, later shown to be 2,5-epoxycyclooct-1-yl acetate (**4a**) and 2,6-epoxycyclooct-1-yl acetate (**4b**).

Anal. Calcd for $C_{10}H_{16}O_3$: C, 65.22; H, 8.69. Found: C, 64.92; H, 8.66.

The mixture of the acetoxy ethers **4a** and **4b** was reduced with lithium aluminum hydride to a mixture of alcohols. The tosylates, prepared by treatment of the alcohols with tosyl chloride in pyridine, were treated with lithium aluminum hydride, giving a mixture of 1,4-and 1,5-epoxycyclooctane[10] in a relative ratio of 40:60 as shown by gas chromatography (column C).

Acknowledgment.—This work was supported in part by grants provided by Research Corp. and the Petroleum Research Fund of the American Chemical Society (PRF 1773-A4). We are grateful to the National Science Foundation for an institutional grant toward the purchase of a Varian A-60 nmr spectrometer, and to J. M. Lodge for her assistance in the initial stages of this problem.

[12] The yield was from gas chromatographic analysis corrected by the use of an internal standard and based on starting material.

[13] The products were isolated by gas chromatography and identified by comparison of their infrared spectra with those of authentic samples, and by their retention times on gas chromatography.

Reaction of Benzoylacetonitrile and α-Benzoylphenylacetonitrile with Acetic Anhydride in the Presence of Boron Trifluoride[1]

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It has been shown that certain β-ketonitriles can be converted in good yields to the corresponding β-ketoamides by means of boron trifluoride in aqueous acetic acid.[2]

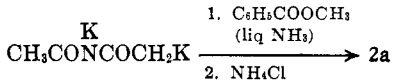
In the present study we have found that two such β-ketonitriles, benzoylacetonitrile (**1a**) and α-benzoylphenylacetonitrile (**1b**), were converted to the respective N-acetyl-β-ketoamides **2a** and **2b**, by a modification of the above procedure in which excess acetic anhydride was added to the reaction mixture. Thus, when **1a** and **1b** were allowed to react with a mixture of acetic anhydride and boron trifluoride–diacetic acid complex (BTDA) at room temperature, **2a** and **2b** were produced in yields of 90 and 82%, respectively (eq 1).

$$C_6H_5COCHRCN \xrightarrow[\text{2. aq } CH_3COONa]{\text{1. } (CH_3CO)_2O\text{, BTDA}} C_6H_5COCHRCONHCOCH_3 \qquad (1)$$

1a, R = H
d, R = C_6H_5

2a, R = H
b, R = C_6H_5

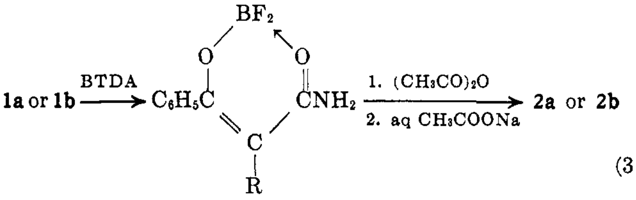
The identity of **2a** was established by comparison with an authentic sample, which was synthesized independently from the dipotassio salt of diacetylimide and methyl benzoate[3] (eq 2). Structual assignment



$$CH_3CO\overset{K}{N}COCH_2K \xrightarrow[\text{2. } NH_4Cl]{\text{1. } C_6H_5COOCH_3 \text{ (liq } NH_3)} \textbf{2a} \qquad (2)$$

2b was based on analysis and spectral studies. The infrared spectrum had N–H absorption at 3.10 μ and carbonyl absorptions at 5.80 and 5.95 μ.[4] The nmr spectrum[5] had singlets at 2.20 and 6.60 ppm for the methyl protons of the N-acetyl group and the methinyl hydrogen, respectively. In addition, there was complex aromatic absorption centered at 7.80 ppm. The integrated intensity of this latter multiplet indicated that the imide proton signal was obscured by the aromatic absorption.

Since Hauser and Eby[2] have demonstrated that their method for conversion of β-ketonitriles to β-ketoamides involves intermediate formation of boron difluoride complexes of the β-ketoamides, it is suggested that the present conversion may involve initial reaction of **1a** and **1b** with BTDA to form boron difluoride complexes **3a** and **3b**,[6] followed by N acetylation of the complexes[7] to afford **2a** and **2b** (eq 3). This sequence was supported



(3)

3a, R = H
b, R = C_6H_5

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[1] Supported in part by the Petroleum Research Fund of the American Chemical Society, Grant No 344-G.

[2] C. R. Hauser and C. J. Eby, *J. Am. Chem. Soc.*, **79**, 725 (1957).

[3] S. D. Work, D. R. Bryant, and C. R. Hauser, *ibid.*, **86**, 872 (1964).

[4] See L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1958, p 221.

[5] The nmr spectrum was obtained on a Varian Associates A-60 spectrometer using dimethyl-d_6 sulfoxide as the solvent and tetramethylsilane as external standard. Peak areas were consistent with the assignments given in the Discussion.

[6] Although we have chosen structures **3a** and **3b** to represent the boron difluoride complexes, other structures are possible and are discussed in ref 2 and 7.

[7] See J. F. Wolfe, C. J. Eby, and C. R. Hauser [*J. Org. Chem.*, **30**, 55 (1965)] for a report of the acetylation of a related boron difluoride complex under similar conditions.