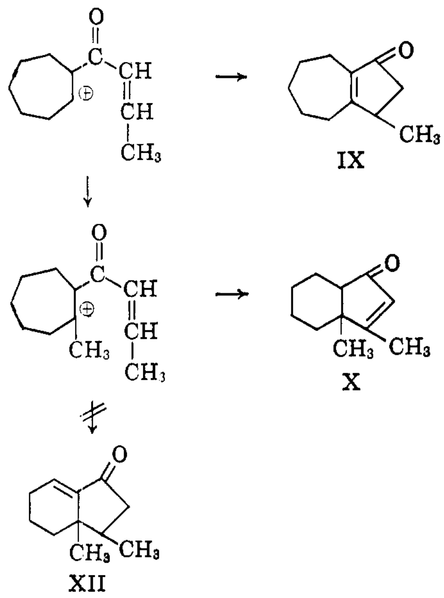
tion and subsequent cyclization. The yield of this product, however, compared with that of the rearranged ketone, X, was low. The structure of the latter, 3,9-dimethylbicyclo[4.3.0]-2-nonen-1-one was based on its ultraviolet, infrared, and nmr spectra. The presence of a vinyl methyl group precluded XII.

The formation of the ketones is visualized as resulting from the following sequence.



Cycloheptyl crotonate (XI) and VII also were isolated in the reaction and are thought to arise from processes similar to those described for I and acetic acid.

Experimental Section

Infrared spectra were measured on a Beckman IR-5 spectrophotometer. Ultraviolet spectra were measured on a Beckman Model DU spectrophotometer in ethyl alcohol solutions. The nmr were measured on a Varian A-60 spectrometer.[13] Thin layer chromatography (tlc) was performed using Camag silica gel without binder. The polyphosphoric acid was obtained from Victor Chemical Co.

Cycloheptene (I) and Acetic Acid Reaction.—Into a 3-necked flask equipped with a condenser, drying tube, and high-torque stirrer was added 9.6 g (0.1 mole) of cycloheptene, 6.0 g (0.1 mole) of acetic acid, and 100 g of polyphosphoric acid. The mixture was stirred for 1 hr in a water bath maintained at 50° and then poured onto approximately 100 g of crushed ice and 100 g of water in order to decompose the complex. After adding 50 g of ammonium sulfate, the aqueous solution was extracted with three 50-ml portions of ether and the ether washed successively with 50 ml of water, two 50-ml portions of 5% ammonium hydroxide solution, and 50 ml of brine. The ether was dried over anhydrous sodium sulfate, evaporated in *vacuo*, and distilled. After a forerun of 2.9 g (31%) of unreacted I, a fraction consisting of 0.75 g (4.8%) of cycloheptyl acetate was obtained, bp 86–88° (18 mm), $n^{26}\mathrm{D}$ 1.4498 [lit.[14] bp 76–78° (11 mm), $n^{20}\mathrm{D}$ 1.4510]. The infrared spectrum of this material was identical with an authentic sample.[14] Hydrolysis with aqueous 10% sodium hydroxide gave cycloheptanol bp 184–185°, $n^{25}\mathrm{D}$ 1.4684 [lit.[15] bp 85–87° (15 mm), $n^{20}\mathrm{D}$ 1.4705]. The second fraction consisted of a mixture of 3.2 g (23.0%) of 2-methyl-1-acetylcyclohexene (IV) and 0.08 g (0.6%) of 2-methyl-3-acetylcyclohexene (V), determined by vapor phase chromatography. The mixture had bp 90–92° (18 mm), $n^{25}\mathrm{D}$ 1.4870 [lit.[16] IV, bp 89.5–90° (17 mm), $n^{25}\mathrm{D}$ 1.4872; V, bp 83–83.5° (17 mm), $n^{25}\mathrm{D}$ 1.4740]. The semicarbazones were prepared and fractionally crystallized from ethanol: IV semicarbazone, mp 226–227° (lit.[16] mp 227–227.5°); V semicarbazone, mp 159–161° (lit.[16] mp 160–162°). Similarly, the 2,4-dinitrophenylhydrazones were obtained from ethanol: IV 2,4-DNP, mp 124–125° (lit.[16] mp 124°); V 2,4-DNP, mp 112–113° (lit.[16] mp 113°). The last fraction consisted of 0.06 g (0.6%) of cycloheptyl cycloheptene (VII), bp 150–152° (17 mm), $n^{25}\mathrm{D}$ 1.5001 [lit.[17] bp 140–141° (12 mm), $n^{20}\mathrm{D}$ 1.5021].

Cycloheptene (I) and Crotonic Acid Reaction.—Following the above procedure, 19.2 g (0.2 mole) of cycloheptene and 17.2 g (0.2 mole) of crotonic acid in 200 g of PPA were allowed to react for 1 hr at 50°. Evaporation of the ether and distillation of the residue gave four fractions. The first fraction consisted of 1.7 g (4.7%) of cycloheptyl crotonate, bp 112–114° (18 mm). Hydrolysis with 10% aqueous sodium hydroxide gave equivalent amounts of cycloheptanol, bp 88–89° (18 mm), $n^{25}\mathrm{D}$ 1.4688 [lit.[15] bp 85–87° (16 mm), $n^{20}\mathrm{D}$ 1.4705] and crotonic acid, mp 71–72° (lit.[18] mp 72°). The second fraction consisted of 5.97 g (18.2%) of a material identified as 3,9-dimethylbicyclo[4.3.0]-2-nonen-1-one (X), bp 128–131° (18 mm), $n^{25}\mathrm{D}$ 1.5033. Vpc showed it to be contaminated with 5% of five other materials. The crude ketone had a $\lambda_{\max}^{\mathrm{EtOH}}$ 226.5 mμ and $\lambda_{\max}^{\mathrm{NaCl}}$ 5.96 μ indicative of the presence of an α,β-unsaturated ketone.[19,20] After unsuccessful attempts to purify the material, the 2,4-dinitrophenylhydrazone was prepared and separated by tlc (3:2 benzene–hexane), mp 157–158°, $\lambda_{\max}^{\mathrm{EtOH}}$ 390 mμ (log ε 4.41). The nmr spectrum was measured in carbon tetrachloride using tetramethyl silane (TMS) as the internal standard. Bands were obtained at δ 1.12 (bridgehead methyl), δ 1.96 (vinyl methyl), and at δ 5.80 (vinyl hydrogen).[21]

Anal. Calcd for $C_{17}H_{20}N_4O_4$: C, 59.29; H, 5.85. Found: C, 59.22; H, 5.92.

The third fraction contained 1.8 g (5.7%) of 3-methylbicyclo-[5.3.0]-9(10)-decen-1-one (IX), bp 144–145° (18 mm), $n^{25}\mathrm{D}$ 1.5117 [lit.[22] bp 140° (15 mm), $n^{20}\mathrm{D}$ 1.5138]. The 2,4-dinitrophenylhydrazone was obtained and recrystallized from ethanol, mp 235–237° (lit.[22] mp 236°). The final fraction contained 0.2 g (1.1%) of VII, bp 150–153° (18 mm), $n^{25}\mathrm{D}$ 1.5000.

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[13] The authors are grateful to Dr. John Oliver for the determination of the nmr spectra.

[14] M. Koblet, P. Barman, V. Prelog, and L. Ruzicka, *Helv. Chim. Acta*, **32**, 256 (1949).

[15] H. Pines, A. Edeleanu, and V. N. Ipatieff, *J. Am. Chem. Soc.*, **67**, 2193 (1945).

[16] R. B. Turner and D. M. Voitle, *ibid.*, **73**, 1403 (1951.)

[17] S. I. Khromov, I. M. Kuznetsova, and E. S. Balenkova, *Zh. Obshch. Khim.*, **26**, 3302 (1956).

[18] M. Julia and J. Bullot, *Compt. Rend.*, **246**, 3648 (1958).

[19] A. R. Gillam and E. S. Stern, "Electronic Absorption Spectroscopy," Edward Arnold Publishers, Ltd., London, 1955, p 92.

[20] K. Nakanishi, "Infrared Absorption Spectroscopy," Holden-Day, Inc., San Francisco, Calif., 1962, p 42.

[21]. L. M. Jackman, "Nuclear Magnetic Resonance Spectroscopy," The Macmillan Co., New York, N. Y., 1959, Chapter 4.

[22] E. A. Braude and W. F. Forbes, *Nature*, **168**, 874 (1951).

Conformational Analysis. VIII.[1,2] Relative Stabilities of 5-Cyanobicyclo[2.2.2]octenes and 5-Acetylbicyclo[2.2.2]octenes

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As part of a continuing effort to determine the relative stabilities of substituted bicyclic compounds,[3] we have sought to relate the factors governing these stabilities to the conformational preferences of substituents in the cyclohexane system. Substituted cyclohexanes have been investigated extensively and the conformational preferences of many substituents are

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[1] Part VII: R. J. Ouellette and G. E. Booth, *J. Org. Chem.*, **31**, 587 (1966).

[2] The authors acknowledge Grant No. 2410-A4 from the Petroleum Research Fund of the American Chemical Society in support of this research.

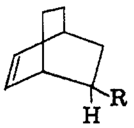
[3] R. J. Ouellette and G. E. Booth, *J. Org. Chem.*, **30**, 423 (1965).

known.[4] The bicyclic compounds are of interest as they are relatively rigid, and consequently the orientations that the atoms can assume are limited. There are numerous possible structural variations, and these compounds could serve as valuable models for the evaluation of nonbonded interactions as a function of distance.

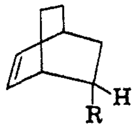
The strain-free 5-substituted bicyclo[2.2.2]octenes, which can be prepared conveniently by the Diels-Alder reaction, are excellent reference compounds and can serve as models for other more strained ring systems. The bicyclo[2.2.2]octene ring skeleton can be constructed readily from Dreiding models without any distortions in the normal bond lengths and angles of carbon–carbon and carbon–hydrogen bonds. Therefore, all the pertinent distances involved in evaluating nonbonded interactions are known. A decrease in ring size in other bicyclic compounds leads to numerous interesting changes in the distances between nonbonded atoms. However, the distances cannot be obtained in an unambiguous manner. The uncertainty arises from a lack of understanding as to how strain energy is structurally accommodated.

The equilibration of the 5-nitrobicyclo[2.2.2]oct-2-enes and 5-carbomethoxybicyclo[2.2.2]oct-2-enes has been reported. In both cases the *endo* isomer is more stable.[3] We now report further studies in the bicyclo[2.2.6]octene systems containing cyano and acetyl groups.

Equilibration of *exo*- and *endo*-5-cyanobicyclo[2.2.2]-oct-2-ene (Ia and IIa) and *exo*- and *endo*-5-acetylbicyclo[2.2.2]oct-2-ene V (Ib and IIb) was accomplished using 0.05 and 0.10 *M* potassium *t*-butoxide in *t*-butyl alcohol. The concentration of the substrates was approximately 0.03 *M*. Since the acidity of the α protons in the compounds examined is low, there should be only a negligible concentration of their conjugate bases present under the equilibration conditions.[5] The effects of kinetic control of protonation of the anion upon work-up should not distort the apparent equilibrium constant.



Ia, R = CN
b, R = $COCH_3$



IIa, R = CN
b, R = $COCH_3$

The equilibrium constants expressed as *exo*/*endo* are independent of the starting isomer and base concentration. The experimental equilibrium constants at 50° are listed in Table I.

In an earlier paper, we reported that both 5-nitrobicyclo[2.2.2]oct-2-ene and 5-carbomethoxybicyclo[2.2.2]oct-2-ene show a clear preference for the *endo* position. The near identity of the equilibrium constants of 0.46 and 0.44 for the *exo*/*endo* ratio of the nitro and carbomethoxy compounds, respectively, suggested that the two substituent groups are of identical effective steric size.

TABLE I

EQUILIBRIUM CONSTANTS FOR THE *endo*- $\rightleftarrows$ *exo*-5-SUBSTITUTED BICYCLO[2.2.2]OCT-2-ENES AT 50°

Substituent	Base, *M*	*K* (*exo*/*endo*)
exo-Cyano	0.10	0.89, 0.88, 0.89
	0.05	0.88, 0.88, 0.88
endo-Cyano	0.10	0.89, 0.89, 0.90
	0.05	0.88, 0.89, 0.89
exo-Acetyl	0.10	0.41, 0.40, 0.41
	0.05	0.40, 0.40, 0.40
endo-Acetyl	0.10	0.41, 0.42, 0.41
	0.05	0.40, 0.41, 0.40

The 5-acetylbicyclo[2.2.2]oct-2-enes and in a less definitive manner, the 5-cyanobicyclo[2.2.2]oct-2-enes also are more stable in the *endo* position. This preference for the *endo* position is undoubtedly a reflection of the unfavorable interaction between a substituent in the *exo* position and the *syn*-7 proton. If the effect of the ethylene bridge in these compounds can be disregarded as unimportant, then the sole controlling structural feature in the determination of the relative stabilities of the substituted bicyclo[2.2.2]octenes is the methylene group at the 7 position. The torsional angles between the substituent in either the *exo* or *endo* position and the bridgehead hydrogen are identical and, therefore, cannot contribute to the relative stabilities of these compounds. In addition, the *exo* substituent is eclipsed by the *exo*-6 hydrogen and the *endo* substituent is eclipsed by the *endo*-6 hydrogen. The torsional angles between either an *exo* or *endo* substituent and the C_6–C_1 bond are identical. Therefore, the only structural features which should lead to a difference in stabilities of the *exo* and *endo* substituents is the 60° torsional angle involved between the *exo* substituent and the 7-methylene group on the one hand and the 60° torsional angle between the *endo* substituent and the vinyl methine group on the other hand.

The distance separating the *syn*-7 proton from the substituent center at the 5 position is identical with that between the 3-axial proton and the substituent in the 1-axial position in cyclohexane compounds. Therefore, the energy of this interaction in the bicyclo[2.2.2]octenes should be one-half that observed in the cyclohexane compounds, where there exists both 3- and 5-*syn*-axial hydrogens as opposed to only one hydrogen of this type in the bicyclo[2.2.2]octenes.

The conformational preferences of the carbomethoxy,[4] nitro,[6] and cyano[4] groups at 50° are 1.2, 1.1, and 0.2 kcal/mole, respectively. The conformational preference of the acetyl group has not been determined, but it would be expected to be in the range of 1.0–1.2 kcal/mole. The differences in free energies between the *exo* and *endo* positions in bicyclo[2.2.2]octenes are 0.55, 0.58, 0.54, and 0.38 at 50° for the carbomethoxy, nitro, acetyl, and cyano groups, respectively. A comparison of both groups of free-energy changes suggests that the above interpretation of the structural features controlling the stabilities of substituted bicyclo[2.2.2]-octenes has some basis in fact. It is difficult to exclude the possibility that the π electrons in the double-bond affect the stability of the *endo* compounds. In addition the *syn*-8 proton which is at a distance of 3.4 A from the *exo* substituent center may exert some in-

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[4] E. L. Eliel, N. L. Allinger, S. J. Argyal, and G. A. Morrison, "Conformational Analysis," John Wiley and Sons, Inc., New York, N. Y., 1965, pp 436–442.

[5] P. Wilder, Jr., and D. Knight, *J. Org. Chem.*, **30**, 3078 (1965).

[6] R. J. Ouellette and G. E. Booth, *ibid.*, **31** 587 (1966).

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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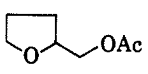
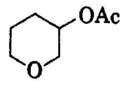
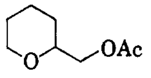
The formation of acetoxy cyclic ethers from the reaction of lead tetraacetate with olefinic alcohols has been reported in aliphatic,[2] bicyclic,[3] and steroidal[4] systems. In an aliphatic system, the position of the double bond plays an important role in determining the course of reaction. Thus, allyl acetate resulted from the reaction of 3-buten-1-ol, whereas 4-penten-1-ol yielded the cyclization products **1** and **2**.



1



2



3

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]	Cyclohexane[b]	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).