bicyclo[4.2.0]octyl *cis*-7-acetate (21%), *trans*-bicyclo[4.2.0]octyl *trans*-7-acetate (17%), and 3-cycloocten-1-yl acetate (57%).

Reaction of *trans*-2-Cycloocten-1-ol with Phenyl Azide. The *trans*-2-cycloocten-1-ol was prepared by the solvolysis of *exo*-8-bromobicyclo[5.1.0]octane in aqueous dioxane as described by Whitham and Wright. In order to obtain reproducible results, it was found necessary to add calcium carbonate as a buffer. The alcohol obtained from 0.46 g of the bromide was allowed to react with 0.29 g of phenyl azide in 25 ml of ether at 25° for 30 min. The solvent was removed using a rotary evaporator and all volatile material was removed by maintaining the residue at 0.1 mm pressure for 20 hr. The red semisolid was characterized as the triazoline adduct of the *trans* double bond. The nmr spectrum had bands at τ 2.65–3.34 (aromatic protons), 5.35–6.27 (unresolved multiplet), 6.27–7.09 (unresolved multiplet), 7.18–9.40 (broad, complex band). The ultraviolet spectrum in hexane showed weak absorption at 310 mμ (n → π^*) and an intense band at 239 mμ (π → π^* band of the phenyl substituent). The infrared spectrum showed the absence of phenyl azide. The mass spectrum had its high mass peak at m/e 217 (P−N$_2$). Other characteristic peaks were at m/e 200 (P − N$_2$ − OH), 126 (P − N$_2$ − C$_6$H$_5$N), 93 (C$_6$H$_5$NH$_2$), and 91 (C$_6$H$_5$N).

Solvolysis of *trans*-Bicyclo[4.2.0]octyl *trans*-7-Tosylate in Buffered Aqueous Dioxane. A solution of 0.22 g of the tosylate in 25 ml of 2:1 dioxane–water (by volume) containing 0.08 g of calcium carbonate was heated to reflux for 32 hr. The solution was diluted with 50 ml of cold water, and repeatedly extracted with small portions of ether. The combined ether extract was dried over anhydrous magnesium sulfate and then concentrated using a rotary evaporator. To the residue was added 15 ml of fresh dry ether containing 0.29 g of phenyl azide. After 15 min at 25°, the solvent was removed under reduced pressure and volatile materials were removed by keeping the residue at 0.1 mm for 25 hr. The red semisolid which remained was characterized as the triazoline adduct of *trans*-3-cycloocten-1-ol. The ultraviolet spectrum in hexane showed weak absorption at 310 mμ and an intense band at 239 mμ. The nmr spectrum showed bands at τ 2.69–3.60, 5.10–6.13, 6.15–7.03, and 7.40–9.40. The mass spectrum was quite similar to that of the previously described adduct and had the characteristic bands listed above.
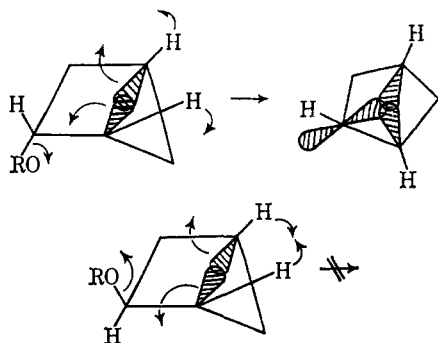
Solvolysis of Bicyclo[2.1.0]pentyl 2-(3,5-Dinitrobenzoates)[1]

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Contribution from the Department of Chemistry, Yale University, New Haven, Connecticut 06520. Received November 8, 1968

Abstract: The rates of solvolysis of *exo*- and *endo*-bicyclo[2.1.0]pentyl 2-(3,5-dinitrobenzoates) have been determined. The *endo/exo* rate ratio is 10^7, and the difference in activation enthalpy is 12 kcal/mole. The results are in accord with an assumption that maximum overlap is required between the developing empty p orbital and the orbitals of the bond being broken for a concerted accelerated solvolysis of a cyclobutyl derivative. The results are compared with those for the series of bicyclo[*m*.2.0]alkyl derivatives.

As a result of our study of the solvolyses of *cis*- and *trans*-bicyclo[4.2.0]octan-7-ol derivatives,[3] it became clear that the opening of the cyclobutyl ring required a specific mode of orbital motion, similar to that required with cyclopropyl derivatives.[4] In an effort to obtain a definitive test of this hypothesis, we have examined the solvolyses of *exo*- and *endo*-bicyclo[2.1.0]-pentyl 2-(3,5-dinitrobenzoates). In the *endo* isomer, the required orbital motion would lead to a decrease in strain and a markedly enhanced rate of reaction should

be found. In the *exo* isomer, the same type of rotation would lead to an increase in strain. Thus, this isomer should have only a reactivity corresponding to a cyclopropylcarbinyl derivative.

Several routes were explored in an effort to obtain the required alcohols. Attempts were made to prepare cyclobutenone ketals by converting 2-bromocyclobutanone to a ketal followed by elimination of hydrogen bromide. The reaction of the bromo ketone with ethylene glycol gave both the dioxolane derivative and the ethylene glycol monoester of cyclopropanecarboxylic acid.[5] Elimination of hydrogen bromide from the dioxolane could not be effected.

Cyclobutenone dimethyl ketal could be prepared by the procedure of Vogel and Hasse[6] which involves the conversion of the Diels–Alder adduct of cyclooctatrienone and dimethyl acetylenedicarboxylate[7] to the dimethyl ketal followed by thermal elimination of the desired ketal. The reaction with diazomethane catalyzed by cuprous bromide proceeded satisfactorily giving the dimethyl ketal of bicyclo[2.1.0]pentan-2-one. Many attempts were made to effect the acid-catalyzed hydrolysis of the ketal. However, in each case the only product was cyclopentenone.[8]

(1) This investigation was supported by Public Health Service Grant GM12800 from the National Institute of General Medical Science.

(2) (a) Taken in part from the Ph.D. Thesis of V. Z. W., 1968; Proctor and Gamble Fellow, 1966–1967; Heyl Fellow, 1967–1968. (b) National Science Foundation Postdoctoral Fellow, 1966–1967.

(3) K. B. Wiberg and J. G. Pfeiffer, *J. Am. Chem. Soc.*, **92**, 553 (1970).

(4) *Cf.* C. H. DePuy, *Accounts Chem. Res.*, **1**, 33 (1968).

(5) These experiments were performed by Dr. R. Cottingham. We wish to thank him for his assistance. The formation of a Favorskii rearrangement product is not too surprising in view of the ease with which 2-bromocyclobutanone undergoes this rearrangement (J. M. Conia and J. L. Ripoll, *Bull. Soc. Chim. France*, 755 (1963)).

(6) E. Vogel and K. Hasse, *Ann.*, **615**, 22 (1958).

(7) A. C. Cope, S. F. Schaeren, and E. R. Trumbull, *J. Am. Chem. Soc.*, **76**, 1096 (1954).
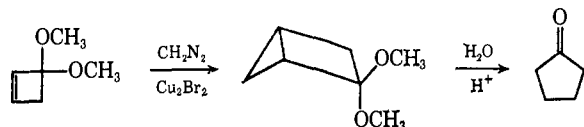
The Diels–Alder adduct mentioned above was then reduced with sodium borohydride to dimethyl tricyclo[4.2.2.0^{2,5}]deca-7,9-dien-3-ol-7,8-dicarboxylate (1). Conversion to the acetate followed by heating gave a mixture of 3-acetoxycyclobutene (2) and trans-1-acetoxybutadiene. Treatment of 2 with diazomethane and cuprous bromide gave a 1:1 mixture of endo- and exo-bicyclo[2.1.0]pentyl 2-acetates which could be converted to the alcohols 3 and 4 by lithium aluminum hydride. The alcohols could be separated by preparative vpc.
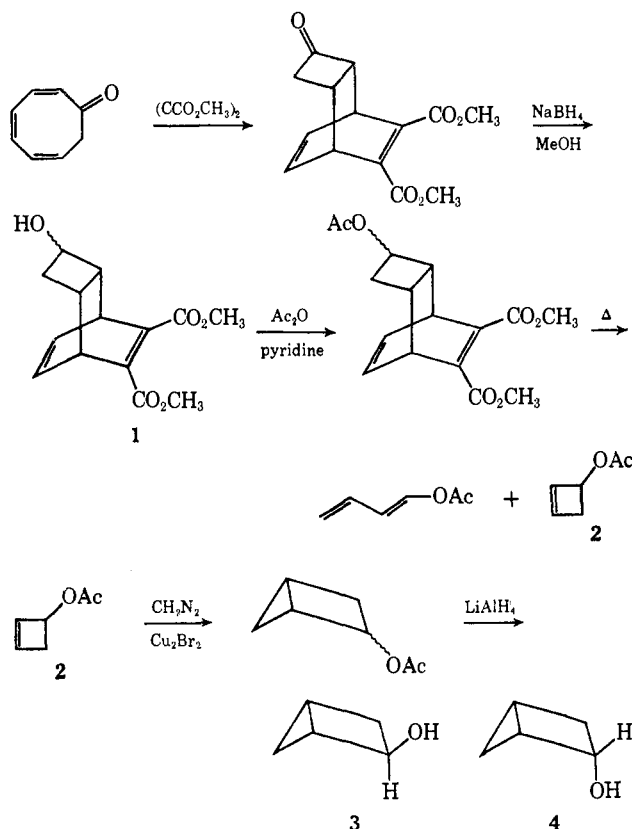
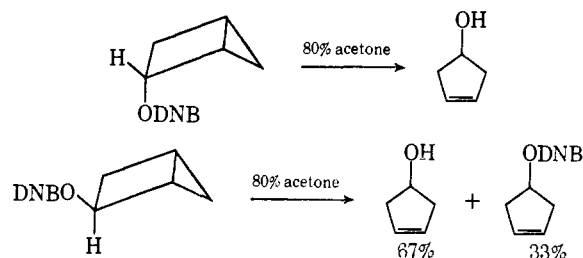
It is possible to assign the location of the hydroxyl group by an analysis of the nmr spectra of the alcohols.[9] The endo isomer had a unique spectrum in which each of the seven hydrogens bonded to carbon led to a separate well-resolved multiplet. The magnitudes of the coupling constants clearly indicated that the hydroxyl group was in the endo position.

The alcohols were converted to the 3,5-dinitrobenzoates. That from the exo isomer was quite stable and easily purified. However, that from the endo isomer was somewhat unstable and partially rearranged to 3-cyclopenten-1-yl 3,5-dinitrobenzoate. The solvolysis products are shown below and the rate constants are summarized in Table I.

The products were determined in 80% acetone and the solvolysis of the exo derivative was studied in that solvent since it is one which is commonly used. However, with the technique necessary to measure the very rapid reaction of the endo derivative, 80% acetone was found to be unsatisfactory.[10] Thus, 80% dioxane was used in this case. The Y values for the two solvents are very close[11] and we estimate that the rate of reaction should be about 17% greater in 80% acetone than in 80% dioxane. This is negligible in comparison to the large difference in reactivity between the two isomers.

It is seen that the endo isomer is remarkably reactive, whereas the exo isomer is less reactive by a factor of 10^7. The rate constants for these compounds are compared with data in the literature in Table II.

The less reactive exo isomer is seen to have a reactivity comparable to that of a typical secondary cyclopropylcarbinyl derivative. The endo isomer has a remarkably high reactivity and is one of the most reactive of the 3,5-dinitrobenzoates which have been studied. The 12 kcal/mole difference in activation enthalpies between the two isomers may be compared with the 26 kcal/mole difference in heat of formation between bicyclo[2.1.0]pentane and cyclopentene.[12] Thus, about half of the total change in strain energy is realized in the activated complex from the endo isomer, indicating that the process described above has proceeded to a large extent by the time the transition state is reached.

The present results also provide an explanation for the changes in reactivity between the members of the bicyclo[m.2.0]alkyl series (Table III). As the second ring is increased in size, the endo/exo ratio decreases until it is essentially unity with the bicyclo[4.2.0]octyl 7-tosylates. The very large exo/endo ratio with the bicyclo[2.1.0]pentyl-2 derivatives results from two factors: the larger degree of strain relief realized when the central bond is cleaved, and the planar geometry of the ring which forces the bridgehead hydrogens toward each other in a concerted reaction of the exo isomer. As the ring size is increased, the strain relief factor decreases, and the geometry improves. Finally, with the bicyclo[4.2.0]octyl derivatives, the cyclobutane ring is probably puckered relieving the bridgehead hydrogen interaction, and the strain relief on cleaving the central

(8) M. Hanack [Suomen Kemistilehti, 39A, 93 (1966)] reported the preparation of the ketal by this method and indicated that the hydrolysis gave both bicyclo[2.1.0]pentan-2-one and cyclopentenone. However, the experimental details have not as yet been reported.

(9) A complete analysis of the spectrum of the endo isomer as well as a partial analysis of that of the exo isomer is given by K. B. Wiberg and D. E. Barth, J. Am. Chem. Soc., 91, 5124 (1969).

(10) In this method [K. B. Wiberg and R. A. Fenoglio, Tetrahedron Letters, 1273 (1963)], a solution of the derivative is added to the solvent containing a known amount of base and an indicator. The time is noted when the indicator changes color. However, the anion of 3,5-dinitrobenzoic acid reacts with acetone in the presence of excess base to give a strongly colored solution.

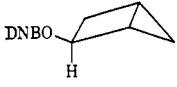(11) E. Grunwald and S. Winstein, J. Am. Chem. Soc., 70, 846 (1948).

(12) The heat of formation of bicyclo[2.1.0]pentane is 37.3 kcal/mole [R. B. Turner, P. Goebel, B. J. Mallon, W. von E. Doering, J. F. Coburn, Jr., and M. Pomerantz, ibid., 90, 4315 (1968)] and that of cyclopentene is 7.9 kcal/mole ["Selected Values of Physical and Thermodynamic Properties of Hydrocarbons," American Petroleum Institute Research Project 44, Carnegie Press, Pittsburgh, Pa., 1952].

Table I. Rates of Solvolysis of *exo-* and *endo*-Bicyclo[2.1.0]pentyl 2-Dinitrobenzoates

Isomer	Solvent	T, °C	k, sec^{-1}	$\Delta H^{\ddagger}$, kcal/mole	$\Delta S^{\ddagger}$, eu
endo	80% dioxane	0.0	$(1.00 \pm 0.02) \times 10^{-3}$	16.9	-10
		21.0	$(1.00 \pm 0.02) \times 10^{-2}$		
		25.0	$1.49 \times 10^{-2\ a}$		
exo	80% acetone	110.0	$(5.40 \pm 0.02) \times 10^{-5}$	28.4	-4
		130.0	$(3.62 \pm 0.03) \times 10^{-4}$		
		25.0	$9.99 \times 10^{-10\ a}$		
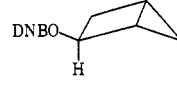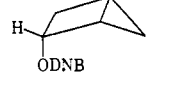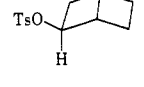
^{a} Extrapolated values.

Table II. Comparison of Rates of Solvolysis of Cyclopropylcarbinyl and Cyclobutyl Derivatives

Compound	k_{25} (80% acetone), sec^{-1}	k_{rel}	Ref
DNBO [structure] H	1×10^{-9}	1	a
H ODNB [structure]	1.5×10^{-2}	10^7	
ODNB [structure]	$\sim 10^{-13}$	10^{-4}	a
[structure] ODNB	3×10^{-8}	30	b
[structure] ODNB	5×10^{-9}	5	c

^{a} Estimated from the rate of acetolysis of cyclobutyl tosylate and an approximate factor of 10^7 for the difference in rate between a tosylate in acetic acid and a dinitrobenz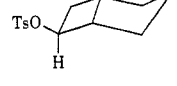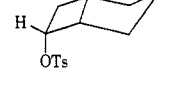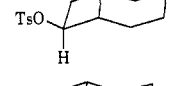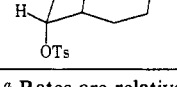oate in 80% acetone. ^{b} L. Birladeanu, T. Hanafusa, B. Johnson, and S. Winstein, *J. Am. Chem. Soc.*, **88**, 2316 (1966). ^{c} K. B. Wiberg and J. Hiatt, *Tetrahedron Letters*, 3009 (1968).

Table III. Comparison of Rates of Solvolysis of Bicyclo[*m*.2.0]alkyl Derivatives

Compound	$k_{rel}{}^a$	k_{endo}/k_{exo}	Ref
DNBO [structure] H	$\sim 10^4$		
		10^7	
H ODNB [structure]	$\sim 10^{11}$		
TsO [structure] H	0.067		13
TsO [structure] H	0.074	460	b
H OTs [structure]	34		b
TsO [structure] H	5.2		
		6.5	3
H OTs [structure]	34		3

^{a} Rates are relative to the corresponding cyclobutyl derivative at 50°. ^{b} H. L. Goering and F. F. Nelson, private communication.

bond has become relatively small. So, here, the *endo/exo* rate ratio is close to unity.

The comparison in Table III permits one to make a prediction concerning the still elusive *endo*-bicyclo-[2.2.0]hexyl-2 derivatives. The *exo* isomer has been found to be quite unreactive and to give products derived from a norbornyl-type rearrangement process.[13] This isomer corresponds to the less reactive bicyclo-[2.1.0]pentyl derivative, except that it does not have the advantage of cyclopropylcarbinyl interaction. The *endo* isomer should be markedly more reactive, and may have a reactivity comparable to the *endo*-bicyclo[2.1.0]-pentyl derivative. This would explain the unusual results found by McDonald and Reineke[14] in their Oppenauer oxidation of *exo*-bicyclo[2.2.0]hexan-2-ol which led to rearrangement. The loss of a hydride ion from the *endo* position would be equivalent to the loss of an ion in a solvolytic process, and would provide the proper stereochemistry for an assisted rearrangement.

Experimental Section

Dimethyl Tricyclo[4.2.2.0^{2,5}]deca-7,9-dien-3-ol-7,8-dicarboxylate. A solution of 161 g (0.615 mole) of dimethyl tricyclo[4.2.2.0^{2,5}]-deca-7,9-dien-3-one-7,8-dicarboxylate[7] in 1300 ml of dry methanol was cooled in an ice bath. To the stirred solution was added 34.0 g (0.90 mole) of sodium borohydride in 2.0-g portions over 1.5 hr. The solution was then stirred at ice bath temperature for 5 hr.

The methanolic solution was acidified to the methyl red end point by the dropwise addition of cold 30% aqueous sulfuric acid solution. The solution was concentrated using a rotary evaporator to a volume of approximately 300 ml and then transferred to a separatory funnel containing 2000 ml of cold water. The aqueous mixture was extracted with one 1000-ml and two 600-ml portions of ether. The combined ether extracts were washed with two 150-ml portions of 3 N sulfuric acid, one 150-ml portion of water, two 100-ml portions of 5% sodium bicarbonate solution, one 100-ml portion of water, and one 100-ml portion of saturated salt solution, and dried over sodium sulfate. The ether was removed using a rotary evaporator leaving 145 g (91%) of a waxy solid, mp 59–62°. Analysis of the product by nmr showed some ether and methanol still in the solid. In fact, recrystallizations from several solvents all gave crystals which had trapped some solvent that could not be removed, even under prolonged vacuum drying.

Dimethyl 3-Acetoxytricyclo[4.2.2.0^{2,5}]deca-7,9-diene-7,8-dicarboxylate. In a 1-l. three-necked flask fitted with a Trubore stirrer with a Teflon paddle, a reflux condenser with a drying tube, and a nitrogen inlet was placed 146 g (0.55 mole) of dimethyl tricyclo[4.2.2.0]-deca-7,9-dien-3-ol-7,8-dicarboxylate, 500 ml of acetic anhydride, and 100 ml of dry pyridine (distilled from barium oxide). The solution was stirred under nitrogen overnight in an oil bath at 90°. The solution was then cooled and poured into a 4-l. beaker containing 2 kg of ice. Solid sodium carbonate was added until the solution was basic to litmus. The mixture was transferred to a 4-l. separatory funnel and extracted with two 500-ml and two 250-ml portions of methylene chloride. The organic layer was washed with one 250-ml portion of 15% potassium hydroxide solution, one 250-ml portion of water, two 500-ml portions of cold 15%

(13) R. N. McDonald and C. E. Reineke, *J. Am. Chem. Soc.*, **87**, 3020 (1965).

(14) R. N. McDonald and C. E. Reineke, *Tetrahedron Letters*, 2739 (1966).

hydrochloric acid solution, one 250-ml portion of water, and one 500-ml portion of saturated salt solution, and dried over sodium sulfate. Removal of the solvent using a rotary evaporator followed by recrystallization of the solid residue from methanol gave 148.5 g (88%) of dimethyl 3-acetoxytricyclo[4.2.2.0^{2,5}]-7,9-diene-7,8-dicarboxylate: mp 110–113°; nmr spectrum τ (CDCl$_3$) 8.25–8.66 (multiplet, 1 H), 8.02 (singlet, 3 H), 6.95–8.00 (multiplet, 3 H), 6.30 (singlet, 6 H), 5.80–6.17 (multiplet, 2 H), 4.87–5.37 (multiplet, 1 H), 3.54–3.75 (multiplet, 2 H).

Anal. Calcd for C$_{16}$H$_{18}$O$_6$: C, 62.7; H, 5.9. Found: C, 62.8, 62.7; H, 5.8, 5.9.

3-Acetoxycyclobutene. A 100-ml three-necked flask was fitted with a magnetic stirrer, a capillary nitrogen inlet which extended to just above the stirrer, and a 15 cm × 1.5 cm Vigreux column connected to an efficient Dry Ice–acetone cooled trap. The size of the nitrogen inlet capillary was such that when a mechanical pump was connected to the trap, the pressure in the apparatus held at 4–5 mm. To the flask was added 40.0 g (0.13 mole) of dimethyl 3-acetoxytricyclo[4.2.2.0^{2,5}]deca-7,9-diene-7,8-dicarboxylate, and the pump was connected. The contents of the flask were heated with stirring for 4 hr using an oil bath at 145°. The temperature was then raised to 175° for 1 hr.

The pot residue was found to be pure dimethyl phthalate. The trap contained 14.2 g (97%) of volatile material. Analysis by nmr indicated 60% 3-acetoxycyclobutene and 40% *trans*-1-acetoxybuta-1,3-diene. The combined products from three runs (40.9 g) were cooled under nitrogen in an ice bath with stirring, and 14.3 g (0.146 mole) of maleic anhydride was added in small portions over 30 min. The ice bath was removed and the solution was stirred at room temperature overnight under nitrogen. The mixture was diluted with 3–4 ml of acetone and placed in a freezer (−17°) to allow the adduct to crystallize. Filtration gave 30.2 g (98%) of the crystalline adduct. The filtrate was taken up in pentane, dried over sodium sulfate, and distilled. 3-Acetoxycyclobutene (24.7 g, 100%) had bp 58° (48 mm). Analysis by vpc indicated less than 1% 1-acetoxybutadiene in the product: nmr spectrum τ (CCl$_4$) 8.06 (singlet, 3 H), 7.56 (doublet with secondary splitting, $J = 13.5$ Hz, 1 H), 7.10 (doublet of doublets, $J = 13.5$, 3.5 Hz, 1 H), 4.77 (multiplet, 1 H), 3.86 (multiplet, 1 H); ir (cm^{-1}) 3065, 2975, 2940, 1740, 1425, 1367, 1260.

Anal. Calcd for C$_6$H$_8$O$_2$: C, 64.3; H, 7.2. Found: C, 64.7, 64.6; H, 7.4, 7.3.

exo- and *endo-***Bicyclo[2.1.0]pentyl 2-Acetates.** The apparatus consisted of a diazomethane generator attached to a reaction vessel. The generator consisted of a 1-l. three-necked flask with smooth joints. A nitrogen inlet tube extended from one side joint to the bottom of the flask. The large center joint was used for the introduction of N-methylnitrosourea, and the remaining joint held an outlet tube which was connected by Tygon tubing to a potassium hydroxide drying tower and from there to a glass tube which extended to just above the stirring bar in the reaction flask. All joints and connections were carefully fire polished. The reaction vessel consisted of a 10-ml erlenmeyer flask with an extended neck to which a side arm had been attached. The neck of the flask held the diazomethane inlet tube and the side arm held an efficient condenser maintained at −10° and a drying tube. The reaction vessel was stirred magnetically.

The generator was charged with 375 ml of 33% potassium hydroxide solution and 50 ml of decalin. The entire apparatus was purged with nitrogen for 15 min. The reaction vessel was then charged with 10.0 g (89 mmoles) of 3-acetoxycyclobutene and 0.3 g of freshly prepared cuprous bromide.[15] The stirrer was started and 2.0 g of N-methylnitrosourea was added to the generator approximately every 20 min while a low nitrogen flow was maintained through the system. During the course of the reaction the solution warmed to 40°.

The reaction was followed by vpc. After 8 hr and 44 g of nitrosomethylurea a 26% conversion was found. Fresh catalyst (0.15 g)

(15) R. N. Keller and H. D. Wycoff, *Inorg. Syn.*, 2, 1 (1946).

was added after every 50 g of nitrosomethylurea, and the generator solution was replaced after 100 g had been added. After 150 g (1.44 moles, 16.2 equiv) of nitrosomethyurea had been added over 22 hr, the reaction was stopped. A 30% conversion was found. Work-up consisted of filtering the reaction mixture through a cake of anhydrous magnesium sulfate and rinsing the flask and the filter cake with boiling pentane.

The product mixture from two reactions was combined. Pentane was removed by distillation through a 30 cm × 1.5 cm glass helix packed column. The concentrated residue was distilled through a 15 cm × 1.5 cm Vigreux column giving 10.4 g (52% recovery) of 3-acetoxycyclobutene, bp 34.5° (16 mm). The residue was distilled through a short-path still giving 5.9 g (54%) of a mixture of *exo-* and *endo*-bicyclo[2.1.0]pentyl 2-acetates, bp 54–62° (16 mm). Vpc analysis indicated the material to be better than 95% pure. However, the *exo* and *endo* isomers could not be separated using any available column. The nmr spectrum indicated a 1:1 mixture of the two isomers.

Anal. Calcd for C$_7$H$_{10}$O$_2$: C, 66.6; H, 8.0. Found: C, 66.9, 67.0; H, 8.3, 8.2.

exo- and *endo-***Bicyclo[2.1.0]pentan-2-ols.** To a stirred solution of 1.9 g (50 mmoles) of lithium aluminum hydride in 125 ml of dry ether which was cooled to −5° was added 5.5 g (44 mmoles) of a mixture of *exo-* and *endo*-bicyclo[2.1.0]pentyl 2-acetates in 40 ml of dry ether over a 15-min period. The solution was stirred for an additional 15 min. To the solution was then added 1.9 ml of water, 1.9 g of 15% potassium hydroxide solution, and 5.7 ml of water in that order. The mixture was filtered and the solid was washed with boiling ether. The ether solution was dried over magnesium sulfate and distilled through a 30 cm × 1.5 cm glass helix packed column to remove the solvent. A residue of 3.5 g (96%) was left.

The isomeric alcohols were separated by preparative vpc on a 20 ft × $^3/_8$ in. Dow Corning 710 Silicone oil column at 115°. The retention times were 16.5 min (*exo*) and 18.5 min (*endo*).

The *exo*-alcohol had an nmr spectrum τ (CCl$_4$) 9.47–9.52 (m, 1 H), 9.10–9.33 (m, 1 H), 8.05–8.47 (m, 4 H), 6.30 (m, 1 H), 5.20 (s, 1 H, concentration dependent); ir (cm^{-1}) 3630, 3580–3100, 3070, 2980, 1325, 1100.

Anal. Calcd for C$_5$H$_8$O: C, 71.4; H, 9.6. Found: C, 71.4, 71.4; H, 9.5, 9.5.

The 3,5-dinitrobenzoate was prepared and after recrystallization from hexane had mp 114.4–115°.

The *endo*-alcohol had an nmr spectrum τ (CCl$_4$) 9.23–9.60 (m, 1 H), 9.02–9.21 (m, 1 H), 8.46–8.96 (m, 2 H), 8.02–8.35 (m, 1 H), 7.47–7.97 (m, 1 H), 5.52–6.18 (m, 2 H, including hydroxyl proton); ir (cm^{-1}) 3620, 3580–3100, 3065, 2980, 1312, 1100.

Anal. Calcd for C$_5$H$_8$O: C, 71.4; H, 9.6. Found: C, 71.0, 71.2; H, 9.4, 9.4.

The 3,5-dinitrobenzoate was prepared in the usual fashion. Attempted recrystallization from hexane gave a mixture of 66% *endo* ester and 34% Δ^3-cyclopentenyl 3,5-dinitrobenzoate. The unrecrystallized ester was used for the kinetic studies.

Solvolysis of *exo-***Bicyclo[2.1.0]pentyl 2-(3,5-Dinitrobenzoate).** In a heavy-walled ampoule was placed 0.75 g of *exo*-bicyclo[2.1.0]pentyl 2-(3,5-dinitrobenzoate) and 75 ml of 80% acetone. The ampoule was sealed and heated at 120° for 12 hr. Work-up in the usual fashion was followed by bulb-to-bulb distillation to isolate the internal return product (0.214 g, 29%) which was identified as Δ^3-cyclopentenyl 3,5-dinitrobenzoate. Analysis of the alcohol fraction on a 10 ft × $^3/_8$ in. 10% Carbowax column at 130° showed only one alcohol peak which was identified as Δ^3-cyclopentenol both by its retention time and its nmr spectrum.

Solvolysis of *endo-***Bicyclo[2.1.0]pentyl 2-(3,5-Dinitrobenzoate).** A mixture containing 0.158 g of *endo*-bicyclo[2.1.0]pentyl 2-(3,5-dinitrobenzoate) and 0.082 g of Δ^3-cyclopentenyl 3,5-dinitrobenzoate was dissolved in 50 ml of 80% acetone and allowed to stand at room temperature for 1 hr. Work-up proceeded as above, and analysis of the alcohol fraction showed only Δ^3-cyclopentenol. The same result was obtained when the solvolysis was carried out in 80% dioxane.