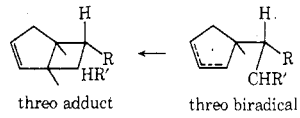

threo adduct threo biradical

to the front. The erythro, threo designations apply to the relative configurations at C_5 and C_6 in the allylic biradical, which are permanently established when the first bond is formed. The radical ends are regarded as corresponding substituents.

(11) L. A. Hull and P. D. Bartlett, *J. Org. Chem.*, **40**, 824 (1975).
(12) L. K. Montgomery, K. E. Schueller, and P. D. Bartlett, *J. Am. Chem. Soc.*, **86**, 622 (1964).
(13) P. D. Bartlett, *Acc. Chem. Res.*, submitted for publication.
(14) D. O. Cowan and R. L. Drisko, *J. Am. Chem. Soc.*, **89**, 3068 (1967).
(15) P. D. Bartlett and L. K. Montgomery, *J. Am. Chem. Soc.*, **86**, 629 (1964).

Synthesis and Solvolytic Studies of Tetracyclo[4.2.0.0^{2,5}.0^{4,7}]octan-3-yl (Secocubane) Derivatives

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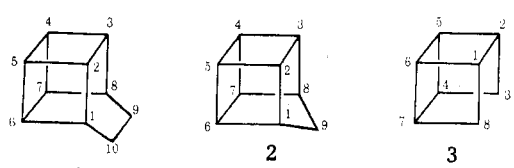
Received October 29, 1974

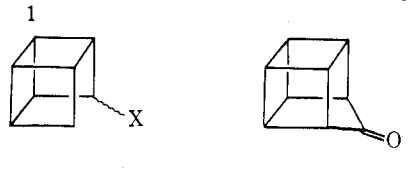
An efficient synthesis of pentacyclo[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]nonan-9-one (**5**, homocubanone) has been devised and its conversion to a variety of tetracyclo[4.2.0.0^{2,5}.0^{4,7}]octan-3-yl (secocubane) derivatives is described. Baeyer–Villiger oxidation of *exo*-secocubyl methyl ketone (**14**) gave the corresponding acetate **15**, which was reduced to exo alcohol **16**. Similar oxidation of *endo*-secocubyl methyl ketone (**13**) gave acetate **18** and trifluoroacetate **19**, shown to have the rearranged *exo*-tetracyclo[4.2.0.0^{2,4}.0^{3,8}]octan-5-yl structure. *exo*-Secocubyl mesylate (**17**) solvolyzed in acetic acid with a rate of $k = 1.27 \times 10^{-4}$ sec^{-1} at 75°, and gave one product, acetate **18**. The results obtained in this investigation are compared with the reactivity of *exo*- and *endo*-bicyclo[2.2.0]hex-2-yl derivatives and explained in terms of controlling steric, geometric, and conformational factors.

The study of strained polycyclic small-ring compounds has become widespread in recent years.[1] In particular, the use of the cubane "cage" compound series pentacyclo[4.4.0.0^{2,5}.0^{3,8}.0^{4,7}]decyl (bishomocubyl), pentacyclo[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}] (homocubyl), and cubane itself has facilitated the study of strain–reactivity relationships. Investigations with derivatives of these cage compounds have given insight into the nature of transition metal catalyzed rearrangements of strained systems,[2] and solvolysis studies of bishomocubyl (**1**)[3] and homocubyl (**2**)[4] derivatives have offered exceptional opportunities for the investigation of transition states, intermediates, and strain release factors in carbonium ion rearrangements.

A natural extension to the studies of cubane-related cage compounds is the tetracyclo[4.2.0.0^{2,5}.0^{4,7}]octyl (secocubane) system (**3**). These solvolytic studies of secocuban-3-yl derivatives (**4**) offer exceptional opportunities for the study of the geometrical and stereochemical requirements of carbonium ion rearrangements in strained systems. The pucker[5,6] of the side cyclobutane rings in the rigid secocubyl cage causes a large stereochemical difference in the rearrangement routes open to the exo and endo isomers of **4**. Furthermore, one would anticipate significant differences in exo vs. endo reactivities in the secocubyl series.



1 2 3



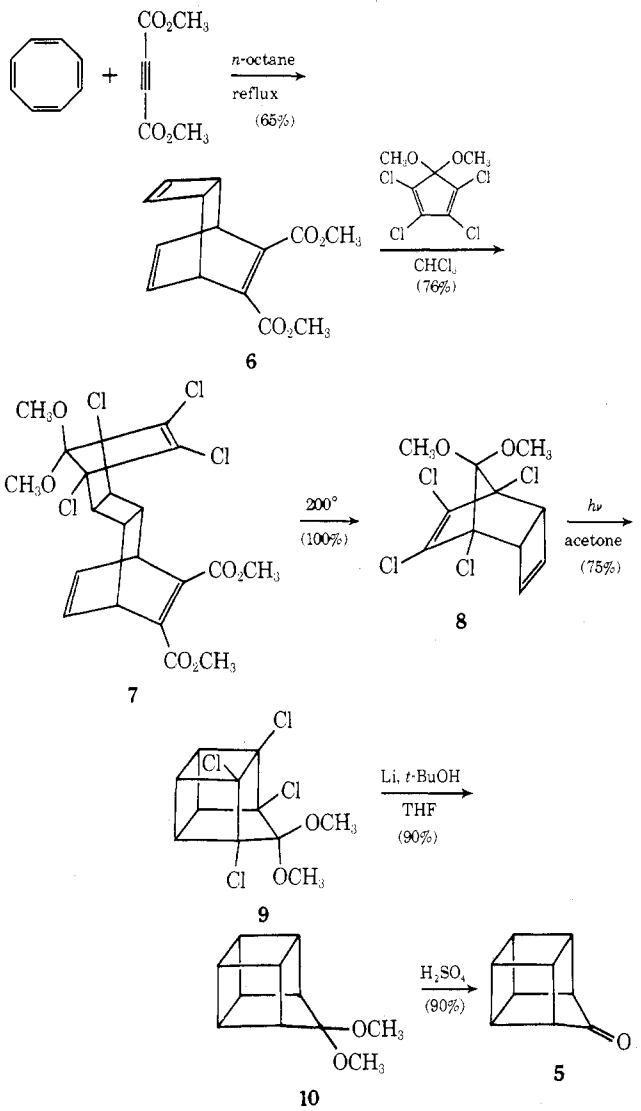
4 5

The discovery of the intramolecular [2 + 2] photocycloaddition reaction has lead to the development of synthetic routes to a variety of polycyclic cage compounds.[7] However, the difficulties which make these compounds such a synthetic challenge often hamper further studies. The multistep, low-yield synthetic routes to homocubanes[8] and secocubanes[9] limit the quantities of material available for solvolytic and other chemical investigations. We now wish to describe the development of a convenient and efficient synthesis of homocubanone (**5**) which makes large quantities of ketone available for use as a synthetic intermediate. We also wish to report, in detail, on the conversion of **5** to monofunctionalized secocuban-3-yl derivatives, and the studies undertaken of the solvolytic reactivity of the secocubane compounds.

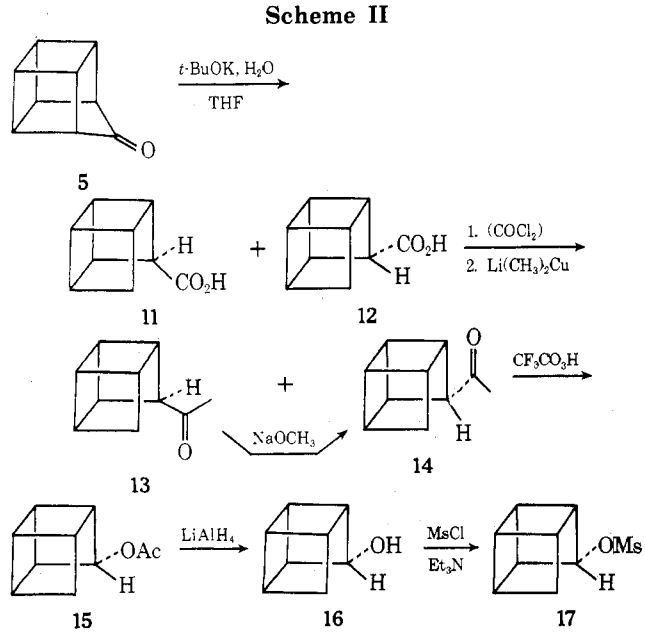
Synthesis. The synthesis of homocubanone was accomplished by the series of reactions outlined in Scheme I. The synthesis of tetrachlorohomocubanone ketal **9** was first reported by Warrener and coworkers;[10] however, no experimental details were given and no attempt was made to optimize the yield. In the present study, it has been found that a 65% yield of **6** could be obtained when the reactants were refluxed in *n*-octane (bp 125°) for 6 days.[11,12] Dechlorination of **9** with lithium metal and *tert*-butyl alcohol in tetrahydrofuran[13] gave homocubanone dimethyl ketal (**10**) in 90% yield. Ketal **10** was hydrolyzed to homocubanone (**5**) with 5% aqueous sulfuric acid. The sequence illustrated in Scheme I represents a 30% overall yield synthesis of **5** from cyclooctatetraene, and is capable of providing 20–30-g quantities of material for further synthetic efforts.

Conversion of **5** to the secocubane system was achieved via nonenolizable ketone cleavage.[14] Thus, when **5** was added to a stirred suspension of potassium *tert*-butoxide and water in tetrahydrofuran, and the mixture was heated at 50° for 6 hr, an 85% yield of a mixture of *endo*-and *exo*-secocubane-3-carboxylic acids (**11** and **12**) in a 9:1 ratio was obtained. The NMR spectrum of the mixture of **11** and **12** contained broad singlet resonances at δ 2.3 for **11** and 2.5 for **12** (in a ratio of 9:1) for the methylene protons and a broad multiplet at δ 3.0–3.7 for the remaining cage protons of both isomers. The upfield shift of the methylene protons of endo isomer **11** is consistent with the results found for

Scheme I



Scheme II



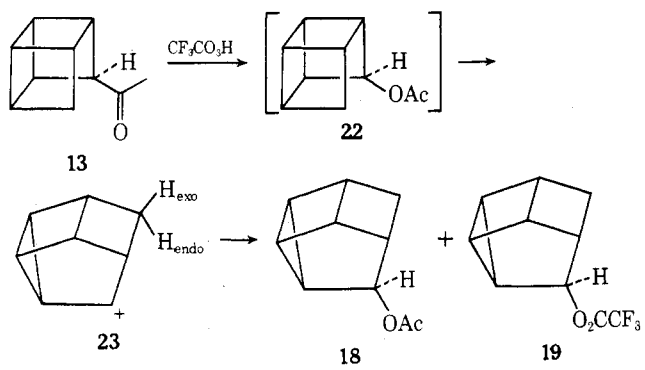
other cage and half-cage compounds, and this shift has been attributed to steric compression in the endo isomer.[15]

The synthetic route to *exo*-secocubane-3-mesylate (**17**) is illustrated in Scheme II. The acid mixture, **11** and **12**, was treated with oxalyl chloride, and the resultant crude acid chloride mixture was converted to a mixture of endo and exo methyl ketones **13** and **14** by treatment with lithium dimethylcuprate.[16] The mixture of methyl ketones was separated by silica gel chromatography, or alternatively, was quantitatively converted to exo isomer **14** by treatment with sodium methoxide in methanol. Baeyer–Villiger oxidation of **14** with trifluorooperacetic acid in buffered methylene chloride[17] gave exo acetate **15** in good yield. Lithium aluminum hydride reduction of **15** gave *exo*-secocuban-3-ol (**16**), which was converted to mesylate **17** in the usual manner.[18]

The NMR spectra of both alcohol **16** and mesylate **17** exhibited the characteristic doublet, J = 2 Hz, at δ 4.85 and 5.55 assigned to the protons α to the alcohol and mesylate group, respectively. In addition, both spectra had similar two-proton multiplets at δ 2.4 for the methylene protons and six-proton multiplets at δ 3.5 for the cage protons. The similarities between the spectra of **16** and **17** indicate that mesylate formation occurred without rearrangement of the cage skeleton.

Results

Baeyer–Villiger oxidation of endo ketone **13** with trifluoroperacetic acid in buffered methylene chloride proceeded at a much slower rate than **14**, presumably owing to steric hindrance in the endo isomer. The reaction gave a 90% yield of approximately equimolar amounts of an acetate **18** and a trifluoroacetate **19** with rearranged carbon skeletons. The acetate and trifluoroacetate had infrared carbonyl absorptions at 1730 and 1780 cm^{-1}, respectively, and both compounds had an ion corresponding to formula C_8H_9 for the parent carbon skeleton fragment in the mass spectrum, isomeric with the secocubyl cage system. The NMR spectra of **18** and **19** were very similar, with a signal for the α-oxy proton at δ 4.75 and 5.0, respectively. Both compounds exhibited broad, complex multiplets at δ 1.6–2.3 and 2.3–2.9, and the acetate had a three-proton singlet at δ 1.95 for the acetate methyl group.



The high-field multiplet at δ 1.6–2.3 is indicative of a fused cyclopropane ring in the rearranged carbon skeleton.[19] The absence of any NMR or infrared evidence for unsaturation suggests that the new structure is still a tetracyclic system. The production of both acetate and trifluoroacetate is consistent with ionization of the first-formed acetate, followed by carbonium ion rearrangement prior to collapse of the products. The equimolar ratio of acetate to trifluoroacetate, formed in spite of the overwhelming excess of trifluoroacetate ion in solution, is indicative of the much greater nucleophilicity of acetate anion and/or internal return of the acetate anion.

Lithium aluminum hydride reduction of the crude mixture of **18** and **19** gave a single alcohol **20**, which was oxi-

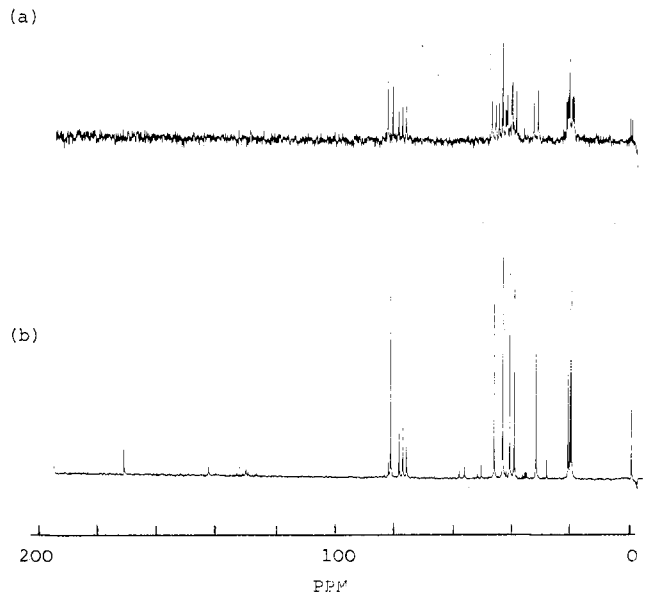
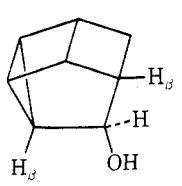


Figure 1. ^{13}C NMR spectrum of solvolysis acetate **18**: (a) off-resonance coupled; (b) wide-band coupled.

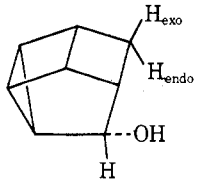
dized with chromium trioxide–pyridine to the corresponding ketone **21**. The ketone had the molecular formula C_8H_8O, determined by high-resolution mass spectroscopy, an infrared carbonyl absorption at 1750 cm^{-1}, and an ultraviolet λ_{max} at 202 nm (ϵ 2500), indicative of a cyclopropyl conjugated ketone.[20]

The above data are consistent with the proposal of a cyclobutyl–cyclopropylcarbinyl rearrangement of the first-formed *endo*-secocubyl acetate (**22**) to the tetracyclo[4.2.0.$0^{2,4}$.$0^{3,8}$]oct-5-yl ring system (**23**). A similar rearrangement of a strained cyclobutyl ketone, carvonecamphor, to a cyclopropylcarbinyl system under Baeyer–Villiger conditions has been reported by Buchi.[21] The formation of both acetate and trifluoroacetate products from rearrangement of **22** under Baeyer–Villiger conditions indicates that a solvated carbonium ion, free of acetate counterion, was formed. For steric reasons, it was expected that nucleophilic attack would give exo products **18** and **19**, due to the endo-methylene hydrogen (H_{endo}), which blocks approach from that side of the molecule.

The exo configuration of **18** and **19** was confirmed by addition of Eu(fod)$_3$ to a solution of alcohol **20** in carbon tetrachloride. The multiplet assigned to the methylene protons of **20** at δ 1.90 moved downfield at a slower rate than the signals for the protons β to the hydroxyl group (H_β) when successive 1-mg portions of Eu(fod)$_3$ were added. Models indicate that the hydroxyl oxygen of endo alcohol **24** would be very close to H_{endo}, and the NMR resonance of



20

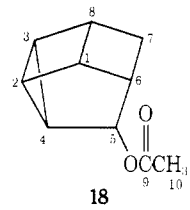


24

the methylene protons of **24** would be expected to separate as the H_{endo} signal was shifted downfield at a rapid rate.

Final proof of the structure of acetate **18** was obtained from its carbon-13 NMR spectrum. The off-resonance decoupled and wide-band decoupled ^{13}C NMR spectra of **18** are shown in Figure 1, and the chemical shifts and assignments of the various resonances are listed in Table I.

Table I
^{13}C NMR Assignments for Solvolysis Acetate 18

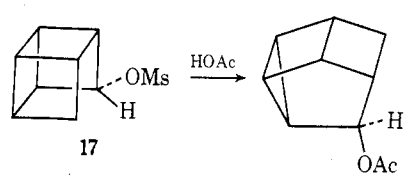


18

Carbon	δ, ppm	Splitting
1	41.0	Doublets
2,3	20.0,20.5	Doublets
4	21.2	Doublet
5	81.3	Doublet
6	46.2	Doublet
7	43.4	Triplet
8	39.4	Doublet
9	171.3	Singlet
10	32.0	Quartet

The presence of three cyclopropyl carbons at δ 20.0–21.2, one methylene carbon at δ 43.4, which appears as a triplet in the off-resonance spectrum (C-7), and the appropriate chemical shifts of the tertiary carbons in relationship to their surroundings confirm the structure of **18**.

When mesylate **17** was stirred for 22 hr in sodium acetate buffered acetic acid at 80°, a quantitative yield of a mixture of acetates was obtained. Analysis of the mixture by VPC showed 90% of one acetate, which proved to be identical with rearranged acetate **18** obtained from Baeyer–Villiger reaction of endo ketone **13**. In addition, trace amounts of several other products were obtained which were not investigated.

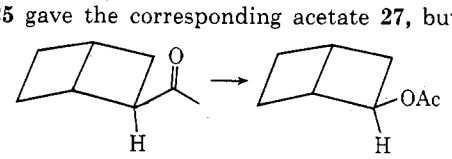


17 **18**

The acetolysis rate of **17** was determined at three temperatures by measuring the disappearance of the NMR signal for the proton α to the mesylate group vs. an internal standard (chloroform). Calculations based on these measurements give first-order rate constants of $k = 1.27 \times 10^{-4}$ sec^{-1} at 75.6°, $k = 2.61 \times 10^{-5}$ sec^{-1} at 60.0°, and $k = 2.95 \times 10^{-6}$ sec^{-1} at 44.7°. Extrapolation to 25° gives $k = 2.5 \times 10^{-7}$ sec^{-1}, $E_a = 30 \pm 3$ kcal/mol, and $\Delta H^{\ddagger} = 27 \pm 3$ kcal/mol.

Discussion

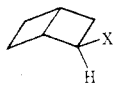
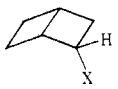
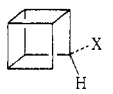
It is instructive to compare the reactivities of secocubyl derivatives with their corresponding bicyclo[2.2.0]hex-2-yl models. McDonald and Davis[22] found that *exo*- and *endo*-2-acetylbicyclo[2.2.0]hexanes (**25** and **26**) exhibited reactivity in the Baeyer–Villiger reaction similar to that of *exo*- and *endo*-secocubyl ketones **14** and **13**. Oxidation of exo ketone **25** gave the corresponding acetate **27**, but similar

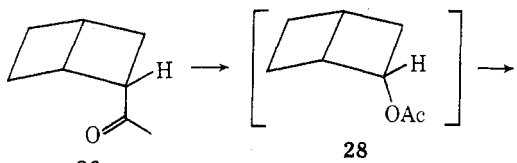


25 **27**

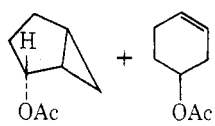
treatment of endo ketone **26** gave a mixture of the expected endo acetate **28**, rearranged acetate **29**, and a trace of **30**.

Table II

Compd	Relative solvolysis rate, X = OSO_2R	Ref
	1.0	23
	8×10^7	24
	9.0	25
	2.3	This study



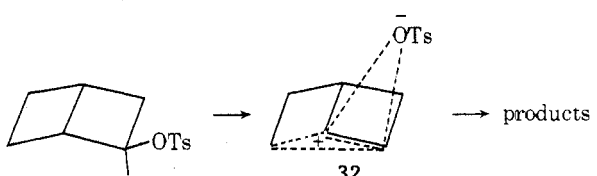
26 28



29 30

Endo acetate **28** underwent further rearrangement on standing at −26° in carbon tetrachloride solution, forming additional **29** and **30.**

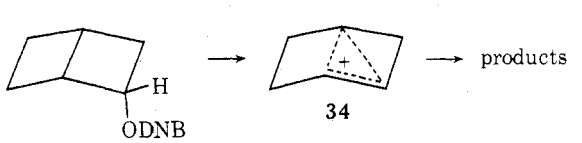
The relative solvolysis rates of the compounds relevant to this study are summarized in Table II. Acetolysis of bicyclo[2.2.0]hex-2-yl tosylate (**31**) proceeded with carbon–carbon bond migration to form ion pair **32,** which collapsed



31 32

to give rearranged tosylate and acetate products.[23] The cyclobutane rings of **31** are nearly planar. Hence, the formation of a stabilized bicyclobutonium ion, such as that generated from cyclobutyl tosylate, is prohibited. Since the solvolysis rate of cyclobutyl tosylate is faster than expected by bond-angle deformation considerations because of the formation of such a nonclassical ion, the fact that **31** solvolyzes only nine times slower than cyclobutyl tosylate is believed to indicate some anchimeric assistance to ionization due to β,γ-bond migration.

Solvolysis of *endo*-bicyclo[2.2.0]hex-2-yl 3,5-dinitrobenzoate (**33**) in aqueous acetone gave a mixture of rearranged

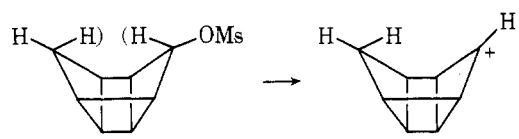


33 34

alcohols and internal returned dinitrobenzoates.[24] The greatly accelerated rate of **33** (Table II) was attributed to the formation of bicyclobutonium ion intermediate **34.**

The large endo/exo rate ratio for the bicyclo[2.2.0]hexyl system is in line with the observed rate ratios for the general series of bicyclo[*m*.2.0]alkyl derivatives.[26] The high solvolytic reactivity of the endo compounds is explained by a disrotatory opening of the central bond to maintain maximum overlap with the developing p orbital at the site of the leaving group. In this manner a bicyclobutonium ion similar to **34** can be formed. A similar mechanism in the exo compounds is prohibited owing to the steric interaction between the opposing bridgehead hydrogens.

In *exo*-secocubyl mesylate (**17**), the side cyclobutanes are puckered, and the leaving group is held in an axial configuration. Hence, **17** should solvolyze at a slow rate relative to cyclobutane.[27] Furthermore, a Wagner–Meerwein rearrangement in **17,** similar to that in **31,** is prohibited by steric and strain factors. Yet the relative solvolysis rate of **17** is the same order of magnitude as **31;** in fact, it is actually somewhat faster. The conformation of **17** prevents any anchimeric assistance to solvolysis, and hence it is unlikely that much, if any, rearrangement occurs during the rate-determining ionization. However, the unexpected rate acceleration can be explained by relief of steric compression of the endo-methylene hydrogens on ionization of **17** to a classical trigonal carbonium ion (**35**). The driving force attributed to such steric compression strain release does account for the observed solvolysis rate, and there is precedent for rate accelerations of solvolyses due to steric compression strain release.[28]



17 35

While rearrangement of **35** to carbonium ion **23** represents a calculated[1c] strain release of approximately 16 kcal, further rearrangements of the cyclopropylcarbinyl carbonium ion could release a great deal more strain energy. It is, therefore, somewhat surprising that the rearrangement sequence stops at **23.** An examination of molecular models indicates that **23** would be expected to be a stable cyclopropylcarbinyl carbonium ion owing to the rigid bisected geometry, and hence a significant barrier to further reaction would be anticipated. The formation of a cyclopropylcarbinyl rearrangement product is also consistent with the rearrangement of *endo*-2-acetylbicyclo[2.2.0]hexane (**26**), which gave mainly cyclopropylcarbinyl acetate product **29.**

The very reactive nature of the endo-secocubyl system is apparent from the results of the present study. Unfortunately, this extreme reactivity has thus far precluded the isolation of an endo-secocubyl derivative for solvolytic studies. However, based on the results of solvolysis studies on the bicyclo[2.2.0]hex-2-yl system, a minimum rate prediction for the endo-secocubyl system would be 10^8 relative to the exo system. Furthermore, the fact that the leaving group in an endo derivative would be equatorial relative to the puckered cyclobutane ring would be expected to enhance the endo/exo rate ratio to an even greater extent.

Experimental Section

Melting points were measured with a Büchi Schmelzpunktbestimmungsapparat, and are uncorrected. Infrared spectra were obtained with a Perkin-Elmer Model 137 spectrometer, and ultraviolet spectra were recorded with a Perkin-Elmer Model 202 spectrometer or a Beckman DK-2A spectrophotometer. Nuclear magnetic resonance spectra were obtained with Varian Model T-60 or HA-100 spectrometers.

Thin layer chromatography (TLC) was done on silica gel coated microscope slides. The plates were sprayed for analysis with a phosphomolybdic acid solution. Analytical vapor phase chromatography was carried out with a Hewlett-Packard Model 5750 research chromatograph and preparative vapor phase chromatography was done on a Wilkins Aerograph, Model A-90-P. Combustion analyses were performed by the Microanalytical Laboratory, and mass spectra were obtained from the Mass Spectroscopy Laboratory, College of Chemistry, University of California, Berkeley.

Technical grade ether distilled from potassium hydroxide and technical grade pentane distilled from phosphorus pentoxide were used for recrystallizations and chromatography. Dry ether was prepared by refluxing reagent grade ether with sodium and benzophenone. Dry tetrahydrofuran was refluxed with and distilled from lithium aluminum hydride. Irradiation grade acetone was refluxed with and distilled from potassium permanganate. All other solvents used were reagent grade unless otherwise specified.

***anti*-Dimethyl Tricyclo[4.2.2.$0^{2,5}$]deca-3,7,9-triene-7,8-dicarboxylate (6).** A solution of 5 g (0.048 mol) of cyclooctatetraene and 6.1 g (0.050 mol) of dimethyl acetylenedicarboxylate in 20 ml of *n*-octane (bp 125°) was refluxed for 6 days under nitrogen. The reaction was followed by the loss of cyclooctatetraene resonance in the NMR spectrum of the reaction mixture. When cyclooctatetraene was almost gone, the reaction was cooled and solvent and unreacted starting material were removed by distillation at aspirator pressure. The residue was distilled at diffusion pump pressure (20 μ) through a short-path distillation apparatus to give 8.7 g of a mixture of adduct **6** and dimethyl phthalate. Careful integration of the NMR spectrum of the mixture showed it to be about seven parts **6** to one part dimethyl phthalate, which indicated a 7.65-g (65%) yield of adduct **6**: bp 80–100° (20 μ) [lit.[11] bp 140–150° (2.0 mm)]; NMR (CCl_4) δ 2.7 (2 H, m, cyclobutene bridgehead), 3.7 (6 H, s, over 2 H, m, esters and bridgeheads), 6.0–6.2 (4 H, m, vinylic); ir (CCl_4) 1740, 1650, and 1600 cm^{-1}. No attempt to obtain the adduct in pure form, free from dimethyl phthalate, was made.

***anti-endo-anti*-Dimethyl 4,5,6,7-Tetrachloro-15,15-dimethoxypentacyclo[8.2.2.$1^{4,7}$.$0^{2,9}$.$0^{7,8}$]pentadeca-5,11,13-triene-11,12-dicarboxylate (7).** A solution of 170 g (0.75 mol) of **6** and 210 g (0.80 mol) of 1,2,3,4-tetrachloro-5,5-dimethoxycyclopentadiene[29] in 400 ml of chloroform was refluxed under nitrogen with constant stirring for 10 days. The solvent was removed by rotary evaporation and the crude solid residue was washed several times with 50% ether–pentane, collected by filtration, and dried under reduced pressure. The combined washings were concentrated and the residue was dissolved in chloroform and refluxed for another 7 days. The total yield of adduct **7** was 290 g (76%): mp 182.5–185.5° (lit.[10] mp 186°); NMR ($CDCl_3$) δ 2.1 (2 H, m), 2.4 (2 H, m), 3.6 and 3.8 (6 H, s, OCH_3), 4.1 (2 H, m), 6.6 (2 H, t, J = 4 Hz, vinylic); ir ($CHCl_3$) 1725, 1640, 1620, and 1200 cm^{-1}; mass spectrum *m/e* 473 (M − Cl).

Anal. Calcd for $C_{21}H_{20}O_6Cl_4$ (510.27): C, 49.40; H, 3.90; Cl, 27.80. Found: C, 49.34; H, 3.80; Cl, 27.92.

***endo*-1,6,7,8-Tetrachloro-9,9-dimethoxytricyclo[4.2.1.$0^{2,5}$]-nona-3,7-diene (8).** Adduct **7**, 237 g (0.465 mol), was pyrolyzed by heating at 200° for 15 min. The resultant oil was chromatographed on 1500 g of silica gel, and elution with 30% ether–pentane gave 145 g (100%) of crude **8**. The crude solid was dissolved in 95% ethanol, decolorized with Norit, and recrystallized to give pure **8**: mp 83.5–84.5° (lit.[10] mp 80–81°); NMR (CCl_4) δ 3.4 (2 H, s, bridgehead), 3.60 and 3.65 (3 H, s, OCH_3), 6.1 (2 H, s, vinylic); ir (CCl_4) 1625 and 1170 cm^{-1}; mass spectrum *m/e* 314, 316, 318.

Anal. Calcd for $C_{11}H_{10}O_2Cl_4$ (316.04): C, 41.75; H, 3.16; Cl, 44.90. Found: C, 41.58; H, 3.08; Cl, 44.74.

1,6,7,8-Tetrachloro-9,9-dimethoxypentacyclo[4.3.0.$0^{2,5}$.$0^{3,8}$.$0^{4,7}$]nonane (9). A solution of 20 (64 mol) of diene **8** in 2 l. of irradiation grade acetone was deaerated with nitrogen and irradiated with a GE-AH6 high-pressure 1000-W mercury vapor lamp. The irradiation was followed by TLC (10% ether–pentane) and was ceased after 18 hr. The solvent was rotary evaporated and the residue was chromatographed on 1500 g of silica gel, eluting with 5% ether–pentane. The product was recrystallized from pentane to yield 15 g (75%) of **9**: mp 143–145° (lit.[10] mp 123°); NMR (CCl_4) δ 3.4–3.8 (6 H, s, on 4 H, m); ir (CCl_4) 3000 and 1200 cm^{-1}; mass spectrum *m/e* 314 (M^+), 279 (M − Cl).

Anal. Calcd for $C_{11}H_{10}O_2Cl_4$ (316.04): C, 41.75; H, 3.16; Cl, 44.90. Found: C, 41.89; H, 3.17; Cl, 44.68.

9,9-Dimethylpentacyclo[4.3.0.$0^{2,5}$.$0^{3,8}$.$0^{4,7}$]nonane (10). A solution of 4.0 g (0.013 mol) of ketal **9** and 8.3 g (0.112 mol) of dry *tert*-butyl alcohol in 70 ml of dry tetrahydrofuran was stirred vigorously under anhydrous conditions and 1.6 g (0.224 mol) of finely cut lithium wire was added. The spontaneous exothermic reaction which ensued was moderated by ice-bath cooling to maintain a gentle reflux. When the reaction subsided the mixture was refluxed for an additional 3 hr and cooled. The mixture was strained (to remove excess lithium) into 500 ml of crushed ice. The aqueous solution was extracted with ether and the ether extracts were dried ($MgSO_4$), filtered, and rotary evaporated to yield 2.1 g (91%) of a colorless oil shown to be almost pure dechlorinated ketal **10** by VPC (SE-30 column, 130°). Short-path distillation gave pure ketal **10**: bp 67–75° (2.0 mm); NMR (CCl_4) δ 3.0–3.55 (8 H, m, cage protons), 3.15 (6 H, s, ketal protons); ir (CCl_4) 2940, 1450, 1100, and 1050 cm^{-1}; mass spectrum *m/e* 178 (M^+), 177 (M − H), 163 (M − CH_3), 147 (M − OCH_3).

Anal. Calcd for $C_{11}H_{14}O_2$ (178.20): C, 74.20; H, 7.87. Found: C, 74.43; H, 7.95.

Pentacyclo[4.3.0.$0^{2,5}$.$0^{3,8}$.$0^{4,7}$]nonan-9-one (Homocubanone, 5). A suspension of 0.46 g (2.58 mmol) of ketal **10** in 25 ml of 5% aqueous sulfuric acid was stirred vigorously at room temperature for 9 hr. A white, crystalline solid gradually formed in the aqueous solution. The solid was extracted with ether, and the ether extracts were washed with 5% aqueous sodium bicarbonate solution until neutral and dried ($MgSO_4$). Solvent was removed by distillation through a short glass helix packed column to yield 0.3 g (88%) of crude homocubanone (**5**). An analytical sample of ketone was obtained by recrystallization from pentane: mp 66–68°; NMR (CCl_4) δ 3.0 (2 H, m, α protons), 3.5 (6 H, m, cage protons); ir (CCl_4) 1760 and 1716 cm^{-1}; mass spectrum *m/e* 132 (M^+).

Anal. Calcd for C_9H_8O (132.17): C, 81.80; H, 6.06. Found: C, 81.5; H, 5.9. There was difficulty with the analysis because of the compound's volatility and its tendency to hydrate readily.

***exo*- and *endo*-Tetracyclo[4.2.0.$0^{2,5}$.$0^{4,7}$]octane-3-carboxylic Acids (11 and 12).** A 300-ml, three-necked flask was fitted with a reflux condenser, a rubber septum inlet, and a nitrogen inlet, and was flushed with nitrogen. A slurry of 32.8 g (0.292 mol) of potassium *tert*-butoxide in 180 ml of dry tetrahydrofuran was introduced, and the flask was cooled in an ice bath. The slurry was stirred magnetically and 1.57 ml (0.087 mol) of water was slowly added via syringe. Homocubanone (3.5 g, 0.026 mol) was added at once, and the mixture was stirred at room temperature for 1 hr and heated at 50° for 6 hr. The mixture was cooled and poured into crushed ice, and the residual salts were washed out with water. The aqueous solution was washed with ether until the washings were colorless, and the aqueous layer was acidified with concentrated hydrochloric acid and extracted with ether. The combined extracts were dried ($MgSO_4$), filtered, rotary evaporated to yield 3.86 g (97%) of a yellow, waxy solid. Sublimation (80°, 0.2 mm) afforded 3.398 g (85% isolated yield) of a mixture of endo and exo acids **11** and **12** which were not separated: NMR ($CDCl_3$) δ 2.3 and 2.45 (2 H, 2 broad s in ratio of 9:1, methylene protons), 3.0–3.7 (7 H, m, cage protons and α-acid proton of endo isomer), 3.6 (1 H, s, α-acid proton of exo isomer); ir ($CHCl_3$) 3600–2500, 1695, and 1265 cm^{-1}; mass spectrum *m/e* 150 (M^+), 105 (M − CO_2H);

Anal. Calcd for $C_9H_{10}O_2$ (150.18): C, 72.00; H, 6.67. Found: C, 71.77; H, 6.69.

***exo*- and *endo*-3-Acetyltetracyclo[4.2.0.$0^{2,5}$.$0^{4,7}$]octane (13 and 14).** A 1.24-g (8.27 mmol) sample of a mixture of endo and exo acids **11** and **12** was dissolved in 50 ml of benzene and an excess (10 g) of oxalyl chloride was added. The mixture was stirred at room temperature for 1 hr and the solvent and excess oxalyl chloride were removed by rotary evaporation to yield a crude acid chloride mixture: ir (CCl_4) 1780 and 1720 cm^{-1}.

A solution of the acid chloride in dry ether was added via syringe to a solution of lithium dimethylcuprate (24.8 mmol) in 150 ml of ether at −78°.[16] The mixture was stirred at −78° for 20 min and hydrolyzed at that temperature with methanol. The mixture was warmed to room temperature and poured into water, and the solution was suction filtered through Celite. The organic layer was separated, the aqueous layer was extracted with ether, and the combined organic layers were washed with saturated salt solution and dried ($MgSO_4$). The solvent was removed by distillation through a glass helix column to yield 1.17 g (95%) of a yellow oil shown by VPC (SE-30 column, 130°) to be a mixture of endo and exo ketones **13** and **14**. The mixture was separated by chromatography on silica gel (10% ether–pentane) to give pure exo ketone **14** and endo ketone **13**. Analytical samples were obtained by preparative VPC (SF-96 column, 135°). Exo isomer **14**: mp 40–42°; NMR (CCl_4) δ 2.1 (3 H, s, methyl), 2.45 (2 H, broad s, methylene), 3.3 (6 H, broad s, cage), 3.65 (1 H, s, α-keto proton); ir (CCl_4) 2940 and 1700 cm^{-1}; mass spectrum *m/e* 148 (M^+), 147 (M − H), 133 (M − CH_3), 105 (M − $COCH_3$).

Anal. Calcd for $C_{10}H_{12}O$ (148.21): C, 81.04; H, 8.16. Found: C, 81.26; H, 8.27.

Endo isomer **13:** mp 35–36°; NMR (CCl_4) δ 2.1 (3 H, s, methyl group), 1.8–2.5 (2 H, m, methylene protons), 2.6–3.8 (7 H, m, cage protons and α-keto proton); ir (CCl_4) 2940 and 1750 cm^{-1}; mass spectrum *m/e* 148 (M^+), 147 (M − H), 133 (M − CH_3), 105 (M − $COCH_3$).

Anal. Calcd for $C_{10}H_{12}O$ (148.21): C, 81.04; H, 8.16. Found: C, 80.73; H, 8.22.

Isomerization of Methyl Ketones 13 and 14. A 2.32-g (0.016 mol) sample of endo ketone **13** was dissolved in 200 ml of anhydrous methanol and a trace of sodium methoxide was added. The mixture was stirred at room temperature under nitrogen for 5 days and poured into 10% aqueous hydrochloric acid, and the solution was extracted with ether. The combined extracts were washed with dilute sodium bicarbonate and dried ($MgSO_4$), and the solvent was removed by distillation to yield 2.19 g (94%) of exo ketone **14,** identical with an authentic sample, as the only product.

***exo*-Tetracyclo[4.2.0.$0^{2,5}$.$0^{4,7}$]octan-3-ol Acetate (15).** To a stirred suspension of 1.9 g (12.8 mmol) of exo ketone **14,** 24 g (167 mmol) of anhydrous disodium phosphate, and 140 ml of methylene chloride was added, dropwise, a methylene chloride solution of trifluoroperacetic acid [prepared from 12.6 ml (85.7 mmol) of trifluoroacetic anhydride]. The mixture was stirred for 1 hr at room temperature and filtered, and the inorganic salts were washed with additional methylene chloride. The combined organic phase was washed with 10% sodium carbonate solution and dried ($MgSO_4$), and the solvent was removed by distillation through a glass helix column to yield 2.036 g (97%) of acetate **15.** An analytical sample was obtained by preparative VPC (SF-96 column, 135°): NMR (CCl_4) δ 2.0 (3 H, s, methyl), 2.3–2.8 (2 H, m, methylene), 3.0–3.6 (6 H, m, cage), 5.5 (1 H, broad s, α-ester proton); ir (CCl_4) 2920, 1730, and 1235 cm^{-1}; mass spectrum *m/e* 164 (M^+), 121 (M − $COCH_3$), 105 (M − OAc).

Anal. Calcd for $C_{10}H_{12}O_2$ (164.21): C, 73.14; H, 7.37. Found: C, 72.90; H, 7.19.

***exo*-Tetracyclo[4.2.0.$0^{2,5}$.$0^{4,7}$]octan-3-ol (16).** Acetate **15,** 2.03 g (12.3 mmol), was reduced with a fivefold excess of lithium aluminum hydride at 0° in dry ether. The solution was hydrolyzed with aqueous ammonium chloride solution and extracted with ether, and the solvent was rotary evaporated to give 1.41 g (94%) of crystalline alcohol **16.** Recrystallization from ether–pentane gave a pure sample of **16:** mp 102–103°; NMR (CCl_4) δ 1.3 (1 H, broad s, hydroxyl proton), 2.0–2.4 (1, H, m, methylene proton), 2.4–2.7 (1 H, m, methylene proton), 2.9–3.7 (6 H, m, cage protons), 4.85 (1 H, d, J = 2 Hz, α-hydroxyl proton); ir (CCl_4) 3600–3100 and 2950 cm^{-1}; mass spectrum *m/e* 122 (M^+), 121 (M − H);

Anal. Calcd for $C_8H_{10}O$ (122.17): C, 78.65; H, 8.25. Found: C, 78.38; H, 8.12.

***exo*-Tetracyclo[4.2.0.$0^{2,5}$.$0^{4,7}$]octan-3-ol Mesylate (17).** A 300-ml, three-necked flask was fitted with a nitrogen inlet and an addition funnel, and was flamed out under nitrogen flush. A solution of 658 mg (5.4 mmol) of alcohol **16** and 688 mg (6.0 mmol) of methanesulfonyl chloride in 60 ml of benzene was added and the flask was placed in an ice bath. The solution was stirred magnetically and 800 mg (8.0 mmol) of triethylamine was added, dropwise, over a period of 2 min. The reaction mixture was removed from the ice bath and stirred at room temperature for 30 min. The mixture was filtered, the salts were washed with additional benzene, and the combined organic solution was rotary evaporated to yield a crude, colorless oil which solidified on standing. The crude residue was dissolved in pentane and concentrated to afford pure crystalline mesylate **17:** 1.04 g (96%); mp 83.5–85°; NMR (CCl_4) δ 2.3–2.8 (2 H, m, methylene), 2.9 (3 H, s, methyl), 3.2–3.9 (6 H, m, cage), 5.55 (1 H, d, J = 2 Hz, α-OMs proton); ir (CCl_4) 2930, 1455, 1210, and 1175 cm^{-1}; mass spectrum *m/e* 105 (M − OMs).

Anal. Calcd for $C_9H_{12}O_3S$ (200.26): C, 53.97; H, 6.04; S, 16.01. Found: C, 53.73; H, 5.96; S, 15.78.

***exo*-Tetracyclo[4.2.0.$0^{2,4}$.$0^{3,8}$]octan-5-acetate (18) and Trifluoroacetate (19) via Baeyer–Villiger Reaction of Endo Ketone 13.** Following the procedure described for the exo ketone **14,** 0.78 g (5.25 mmol) of ketone **13** was oxidized, and after stirring for 1 hr at room temperature, the mixture was refluxed for 5 hr. The solvent was removed by distillation through a glass helix column to yield 0.98 g of yellow oil. VPC (SE-30 column, 120°) examination of the product mixture showed two equal-intensity peaks accounting for about 90% of the material and several components present in small quantities. Preparative VPC (SF-96 column, 130°) of the two major components of the mixture afforded pure samples of acetate **18** and trifluoroacetate **19.** Acetate **18:** NMR (CCl_4) δ 1.5–2.2 (6 H, m, cyclopropyl and methylene), 1.95 (3 H, s, methyl), 2.3–2.9 (2 H, m, bridgehead), 4.75 (1 H, m, α-ester); ir (CCl_4) 3020, 2930, 1725, and 1240 cm^{-1}; mass spectrum *m/e* 164 (M^+), 121 (M − $COCH_3$), 105 (M − OAc);

Anal. Calcd for $C_{10}H_{12}O_2$ (164.21): C, 73.14; H, 7.37. Found: C, 73.00; H, 7.29.

Trifluoroacetate **19:** NMR (CCl_4) δ 1.6–2.4 (6 H, m, cyclopropyl and methylene), 2.4–2.9 (2 H, m, bridgehead), 5.0 (1 H, m, α-ester); ir (CCl_4) 3020, 2930, 1780, and 1155 cm^{-1}; mass spectrum *m/e* 218 (M^+), 105 (M − CO_2CF_3).

Reduction of the Rearranged Acetate 18–Trifluoroacetate 19 Product Mixture from Ketone 13. Formation of Rearranged Alcohol 20. A 1.1-g (ca. 5.8 mmol) portion of crude product mixture from the Baeyer–Villiger reaction on endo ketone **13** was reduced with excess lithium aluminum hydride at 0° in ether. The crude mixture was hydrolyzed with aqueous ammonium chloride and extracted with ether. Solvent was removed by distillation through a glass helix column to yield 0.50 g (70% from the ketone) of crude alcohol **20.** Recrystallization, sublimation, and column chromatography failed to produce pure **20.** However, a pure sample was obtained by preparative VPC (SF-96 column, 120°): NMR δ 1.45 (1 H, s, OH), 1.4–1.8 (4 H, m, cyclopropyl), 1.8–2.1 (2 H, m, methylene), 2.3 and 2.6 (1 H, m, bridgeheads), 3.95 (1 H, m, α-hydroxyl proton); ir (CCl_4) 3600–3100, 3020, 2930, and 1060 cm^{-1}; mass spectrum *m/e* 122 (M^+), 121 (M − H), 105 (M − OH).

Oxidation of Rearranged Alcohol 20. Formation of Ketone 21. A 100-ml, three-necked flask was flamed out under nitrogen flush and a solution of 1.58 g (20 mmol) of dry pyridine was added. The solution was stirred magnetically and 1.0 g (10 mmol) of chromium trioxide (dried over phosphorus pentoxide) was added. The mixture was stirred for 15 min to form the chromium trioxide–bispyridine complex and 200 mg (1.64 mmol) of crude alcohol **20** was added. The mixture was stirred at room temperature for 1 hr and filtered, and the residual tar was washed with several portions of ether. The combined filtrates were washed with 5% sodium hydroxide solution until the washings were colorless, 5% hydrochloric acid, saturated sodium bicarbonate, and saturated sodium chloride solutions. The organic phase was dried ($MGSO_4$), and the solvent was removed by distillation through a glass helix column to yield 110 mg (55%) of a colorless oil. VPC (SE-30 column, 100°) examination of the product mixture showed 90% of one component, ketone **21,** which was purified by preparative VPC (SF-96 column, 120°): nmr (CCl_4) δ 1.4–2.0 (3 H, m, cyclopropyl), 2.1–2.5 (3 H, m, methylene and α-keto), 2.85 (2 H, m, bridgehead); uv max (CH_3OH) 202 nm (ϵ 2500); ir (CCl_4) 3020, 2930, and 1750 cm^{-1}; high-resolution mass spectrum *m/e* 120.0577 (C_8H_8O), 91.0545 (C_7H_7).

Preparative Acetolysis of *exo*-Tetracyclo[4.2.0.$0^{2,5}$.$0^{4,7}$]octan-3-ol Mesylate (17). Mesylate **17** (972 mg, 4.86 mmol) and 480 mg (5.86 mmol) of anhydrous sodium acetate were dissolved in 100 ml of dry acetic acid. The solution was stirred and heated to 80° for 22 hr, cooled, and poured into 500 ml of water. The solution was extracted with pentane twice and with ether once, and the combined extracts were washed with saturated sodium bicarbonate until the extract was neutral. The extract was dried ($MgSO_4$), and the solvent was removed by distillation through a glass helix column to yield 812 mg (100%) of a clear oil. This oil was examined by VPC (SE-30 column, 120°) and was found to consist of 90% acetate **18,** identical with an authentic sample.

Determination of the Acetolysis Rate of Mesylate 17. Approximately 0.5 ml of a solution of 69.3 mg (0.346 mmol) of mesylate **17** and 30 mg (0.364 mmol) of anhydrous sodium acetate in 2 ml of dry acetic acid was placed in an NMR sample tube. Two drops of chloroform was added and the tube was sealed under nitrogen atmosphere. The tube was placed in a constant-temperature bath at 75.6° and the solvolysis was followed by NMR by measuring the decrease of the α-mesylate proton signal at δ 5.55 against the internal standard chloroform signal, using repeated integration technique (error 5%). The rate calculated by computer using a least-squares analysis was 1.2×10^{-4} sec^{-1}.

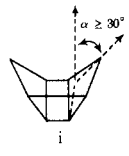
Similar rate determinations were made at 60.0 and 44.7° and gave rates of 2.61×10^{-5} and 2.95×10^{-6} sec^{-1}, respectively. Good first-order plots were obtained in all three cases. These data give $E_a = 30 \pm 3$ kcal/mol and $\Delta H = 27 \pm 3$ kcal/mol.

Acknowledgment. This work was supported by the National Science Foundation (Grant No. GP-8700). L.N.R. expresses appreciation to the National Science Foundation for a predoctoral fellowship.

Registry No.—**5**, 15291-18-6; **6**, 25157-95-3; **7**, 54020-24-5; **8**, 20379-80-0; **9**, 20792-01-2; **10**, 53993-24-1; **11**, 53993-25-2; **12**, 54053-43-9; **13**, 53993-26-3; **14**, 54053-44-0; **15**, 53993-27-4; **16**, 53993-28-5; **17**, 53993-29-5; **18**, 53993-30-9; **19**, 53993-31-0; **20**, 53993-32-1; **21**, 53993-33-2; cyclooctatetraene, 629-20-9; dimethyl acetylenedicarboxylate, 762-42-5; 1,2,3,4-tetrachloro-5,5-dimethoxycyclopentadiene, 2207-27-4; oxalyl chloride, 79-37-8; trifluoroperacetic acid, 359-48-8; methanesulfonyl chloride, 124-63-0.

References and Notes

(1) For review articles in this field see (a) D. Seebach, *Angew. Chem., Int. Ed. Engl.*, **4**, 121 (1965); (b) L. N. Ferguson, *J. Chem. Educ.*, **46**, 404 (1969); (c) ibid., **47**, 46 (1970).
(2) (a) L. Cassar, P. E. Eaton, and J. Halpern, *J. Am. Chem. Soc.*, **92**, 3515 (1970); (b) W. G. Dauben and A. J. Kielbania, Jr., ibid., **93**, 7345 (1971).
(3) W. G. Dauben and D. L. Whalen, *J. Am. Chem. Soc.*, **93**, 7244 (1971).
(4) (a) P. v. R. Schleyer, J. J. Harper, G. C. Dunn, V. J. DiPasquo, and J. R. E. Hoover, *J. Am. Chem. Soc.*, **89**, 698 (1967); (b) J. C. Barborak and R. Pettit, *ibid.*, **89**, 3080 (1967).
(5) The pucker, α, in the secocubyl system is calculated from X-ray studies[6] on secocubyl derivatives to be greater than 30° (i).



i

(6) B. G. DeBoer and D. H. Templeton, personal communication.
(7) For an excellent review see W. L. Dilling, *Chem. Rev.*, **66**, 384 (1964).
(8) (a) W. G. Dauben and D. L. Whalen, *Tetrahedron Lett.*, 3743 (1966); (b) G. L. Dunn, V. J. DiPasquo, and J. R. E. Hoover, ibid., 3737 (1966); (c) R. L. Cargill and T. Y. King, ibid., 409 (1970).
(9) (a) C. G. Chin, H. Cuts, and S. Masamune, *Chem. Commun.*, 880 (1966); (b) W. G. Dauben, C. H. Schallhorn, and D. L. Whalen, *J. Am. Chem. Soc.*, **93**, 1446 (1971).
(10) C. M. Anderson, J. B. Bremner, I. W. McCoy, and R. N. Warrener, *Tetrahedron Lett.*, 1255 (1968).
(11) The established procedure for the preparation of **6** gave the reported yields of only 50%: (a) W. Reppe, O. Schlichting, K. Klager, and T. Toepel, *Justus Liebigs Ann. Chem.*, **560**, 1 (1948); (b) M. Avram, C. D. Nenitzescu, and E. Marica, *Chem. Ber.*, **90**, 1857 (1957); (c) E. E. Van Tamelen and B. C. T. Pappas, *J. Am. Chem. Soc.*, **93**, 6111 (1971). Recently an 82% yield preparation of **6** was reported.[12]
(12) A. G. Anderson, Jr., and D. R. Fagerburg, *Tetrahedron*, **29**, 2973 (1973).
(13) P. Bruck, D. Thompson, and S. Winstein, *Chem. Ind. (London)*, 405 (1960).
(14) P. G. Gassman, J. T. Lamb, and F. V. Zalar, *J. Am. Chem. Soc.*, **89**, 946 (1967).
(15) S. Winstein, P. Carter, F. A. L. Anet, and A. J. R. Bourn, *J. Am. Chem. Soc.*, **87**, 5247 (1965).
(16) G. H. Posner and C. E. Whitten, *Tetrahedron Lett.*, 4647 (1970).
(17) W. D. Emmons and G. B. Lucas, *J. Am. Chem. Soc.*, **77**, 2287 (1955).
(18) (a) J. F. King and T. Durst, *J. Am. Chem. Soc.*, **86**, 287 (1964); (b) W. E. Truce, R. W. Campbell, and J. R. Norell, ibid., **86**, 288 (1964).
(19) R. M. Coates and J. L. Kirkpatrick, *J. Am. Chem. Soc.*, **92**, 4883 (1970).
(20) W. G. Dauben and G. H. Berezin, *J. Am. Chem. Soc.*, **89**, 3449 (1967).
(21) G. Büchi and I. M. Goldman, *J. Am. Chem. Soc.*, **79**, 4741 (1957).
(22) R. N. McDonald and G. E. Davis, *J. Org. Chem.*, **34**, 1916 (1969).
(23) R. N. McDonald and C. E. Reineke, *J. Org. Chem.*, **32**, 1878 (1967).
(24) R. N. McDonald and G. E. Davis, *J. Am. Chem. Soc.*, **94**, 5078 (1972).
(25) H. C. Brown and G. Ham, *J. Am. Chem. Soc.*, **78**, 2735 (1956).
(26) K. B. Wiberg, B. A. Hess, Jr., and A. J. Ashe III in "Carbonium Ions", Vol. 3, G. E. Olah and P. v. R. Schleyer, Ed., Interscience, New York, N.Y., 1968, Chapter 26.
(27) K. B. Wiberg, R. A. Fenoglio, V. Z. Williams, Jr., and R. W. Ubersax, *J. Am. Chem. Soc.*, **92**, 568 (1972).
(28) (a) P. D. Bartlett and M. Stiles, *J. Am. Chem. Soc.*, **77**, 2806 (1955); (b) P. D. Bartlett and T. T. Tidwell, ibid., **90**, 4421 (1968); (c) J. Slutsky, R. C. Bingham, P. v. R. Schleyer, W. C. Dickson, and H. C. Brown, ibid., **96**, 1969 (1974); (d) A. Streitwieser, "Solvolytic Displacement Reactions", McGraw-Hill, New York, N.Y., 1962, p 92.
(29) J. S. Newcomer and E. T. McBee, *J. Am. Chem. Soc.*, **71**, 946 (1949).

Rearrangements of 1,2,3,4-Tetrachloropentacyclo[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]nonan-9-one[1]

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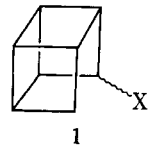
Received November 1, 1974

9,9-Dimethoxy-1,2,3,4-tetrachloropentacyclo[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]nonane (**2**) was found to rearrange to cage-opened ketone **4** on treatment with concentrated sulfuric acid, but, with hydrogen bromide in acetic acid, ketal **2** was hydrolyzed to tetrachlorohomocubane (**3**). Treatment of **3** with aqueous base gave rise to the oxahomocubane acid **6**, while treatment with sodium hydroxide in benzene gave tetrachlorosecocubane acid (**8**). The conversion of **3** to **6** was shown to proceed through **8** via a sequence of intramolecular chlorine displacements by the isolation of intermediate lactone **10**. These results are discussed in relation to reactions of similar compounds which have been previously described in the literature.

As part of an investigation of the tetracyclo[4.2.0.0^{2,5}.0^{4,7}]octane (secocubane) ring system, various chlorinated cage compound intermediates have been studied in an attempt to devise an efficient synthetic route to secocuban-5-yl derivatives (**1**). The chemistry of polycyclic cage compounds is altered a great deal owing to the electron-withdrawing inductive effects and to the steric effects of multiple chlorine substitution,[3] and in the present study attention has been directed toward the role of these two effects upon the rearrangement pathways of the cage system.



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Tetrachlorohomocubanone ketal (**2**) was prepared in good yield by the method of Warrener and coworkers.[4] Attempts to hydrolyze ketal **2** with various concentrations of sulfuric acid (up to 75% acid at temperatures up to 80°) were unsuccessful, the ketal being recovered quantitatively. However, treatment of **2** with concentrated sulfuric acid at room temperature gave an unsaturated ketone **4**, which was isomeric with the expected cage ketone **3**, in 70% yield. The infrared absorption of the product at 1750, 1625, and 1590 cm^{-1} was compatible with an α-chloro conjugated carbonyl group and an additional chlorinated cyclobutene double bond.[5] The ultraviolet spectrum, λ_{max} 234 nm (ϵ 6700), also indicated a conjugated ketone. The NMR spectrum exhibited multiplets at δ 3.6 and 3.4 in a ratio of 2:1 in addition to a one-proton doublet at δ 7.7. Double irradiation of the signal at δ 3.6 caused the δ 7.7 doublet to collapse to a singlet.

The above data indicate cage-opening rearrangement of a hydrolysis intermediate with carbonium ion character at the carbonyl carbon to give the product, 3,4,6,8-tetrachlorotricyclo[4.3.0.0^{2,5}]nona-3,8-dien-7-one (**4**). One possible mechanism for the rearrangement to **4** is illustrated in Scheme I. The driving force behind the indicated 1,3-sigmatropic shift is not clear, but such a shift is necessary in