1-*n*-Butyl-2,6-dimethyl-1,4-dihydropyridin-4-ylideneacetone (27). A solution of 164 mg (1 mmol) of **12a** in 5 ml of $BuNH_2$ was refluxed for 8 hr. The excess of $BuNH_2$ was removed at low pressure and the residue was dissolved in petroleum ether–EtOAc. On cooling (Dry Ice–acetone), 153 mg (70%) of **27** precipitated and as collected by filtration.

Methyl 2,6-Hexadeuteriodimethyl-4*H*-pyran-4-ylidenenitroacetate. To a solution of 215 mg (1 mmol) of **6** in 8 ml MeOD, 4 drops of D_2SO_4 was added, and the solution was kept at 50° for 72 hr. On cooling (Dry Ice–acetone), 200 mg (90%) of product separated and was collected by filtration. The nmr spectrum of the product indicated exchange of about 50% of the methyls' hydrogens by deuterium. The product was redissolved in 8 ml of MeOD containing 4 drops of D_2SO_4, and the reaction mixture was maintained at 50° for an additional 100 hr. Upon cooling, 180 mg (70%) of product was obtained, mp 109°, which was more than 95% hexadeuterated (nmr).

Registry No.—**1**, 1004-36-0; **2**, 1073-80-9; **5**, 49810-66-4; **5a**, 49810-67-5; **6**, 49810-68-6; **7**, 49810-69-7; **8**, 49810-70-0; **8a**, 39588-78-8; **9**, 3280-35-1; **9a**, 49775-27-1; **9a′**, 49810-73-3; **10**, 49810-74-4; **11**, 49810-75-5; **12**, 49810-76-6; **12a**, 39588-76-6; **13**, 49810-78-8; **13a**, 49775-28-2; **14**, 49810-79-9; **15**, 49810-80-2; **16**, 49810-81-3; **17**, 49810-82-4; **18**, 49810-83-5; **19**, 49810-84-6; **19a**, 49810-85-7; **20**, 49775-29-3; **21**, 49810-86-8; **22**, 49810-87-9; **22a**, 49810-88-0; **23**, 49810-89-1; **24**, 49810-90-4; **25**, 49810-91-5; **26**, 49810-92-6; **27**, 49810-93-7; **28**, 28286-88-6; **29**, 49810-95-9; 1-nitro-2-propanone, 10230-68-9; nitromethane, 75-52-5; methyl nitroacetate, 2483-57-0; nitroacetonitrile, 13218-13-8; methyl-3-oxobutyric acid, 105-45-3; methyl acetate, 79-20-9; 3-oxobutyronitrile, 2469-99-0; acetonitrile, 75-05-8; acetonitrile-*d*, 26456-53-1; methylcyanoacetic acid, 105-34-0; 2-cyanoacetamide, 107-91-5; 2,4-pentanedione, 123-54-6; acetone, 67-64-1; malononitrile, 109-77-3; butylamine, 109-73-9; methyl 2,6-hexadeuteriodimethyl-4*H*-pyran-4-ylidenenitroacetate, 49810-96-0.

References and Notes

(1) (a) F. Eiden, *Naturwissenschaften*, **47**, 61 (1960); (b) B. Foelish and D. Krockenberger, *Chem. Ber.*, **101**, 3990 (1968); (c) D. Lloyd and F. J. Wasson, *Chem. Ind.* (*London*) 1559 (1963); *J. Chem. Soc. C*, 1086 (1966); (d) G. Seitz, *Angew. Chem., Int. Ed. Engl.*, **8**, 478 (1969); (e) J. A. Berson, E. M. Evleth, and Z. Hamlet, *J. Amer. Chem. Soc.* **87**, 2887 (1965); (f) C. V. Boyd and L. M. Jackman, *J. Chem. Soc.*, 548 (1963).

(2) (a) R. Mayer, W. Broy, and R. Zahradnik, *Advan. Heterocycl. Chem.*, **8**, 243 (1967); (b) H. C. Smitherman and L. N. Ferguson, *Tetrahedron*, **24**, 923 (1968), and references therein.

(3) J. Chauvelier, *Ann. Chim.* (*Paris*), **3** [12], 393 (1948).

(4) D. Farcasiu, *Rev. Roum. Chem.*, **9**, 865 (1965); *Chem. Abstr.*, **63**, 11480 (1965).

(5) M. Ohta and H. Kato, *Bull. Chem. Soc. Jap.*, **32**, 707 (1959).

(6) L. L. Woods, *J. Amer. Chem. Soc.*, **80**, 1440 (1958).

(7) W. E. Mathews and D. G. Kubler, *J. Org. Chem.*, **25**, 266 (1960).

(8) (a) K. Dimroth and K. H. Wolf, *Angew. Chem.*, **72**, 777 (1960); (b) H. Kato, T. Ogawa, and M. Ohta, *Bull. Chem. Soc. Jap.*, **33** 1467 (1960); (c) F. Eiden, *Arch. Pharm.*, **293**, 404 (1960); **295**, 607 (1962).

(9) H. Strzlecka, M. Dupre, and M. Simalty, *Tetrahedron Lett.*, 617 (1971).

(10) Other possible isomeric structures of **9a** which may possibly result from ring opening **9**, cleavage of the acetyl moiety and recyclization do not fit the chemical and physical properties of **9a**.

(11) See, *e.g.*, ref 9.

(12) P. Beak and C. A. Carls, *J. Org. Chem.*, **29**, 2678 (1964).

(13) P. Bellingham, C. D. Johnson, and A. R. Katritzky, *J. Chem. Soc. B*, 866 (1968).

(14) Although diastereotopic, the two ring methyls at C-2 and C-6 always exhibit one broad signal which is probably due to the relatively small anisotropy experienced by these groups of protons.

(15) C. D. Hurd and M. E. Nilson, *J. Org. Chem.*, **20**, 927 (1955).

(16) H. Feuer, H. B. Hass, and K. S. Warren, *J. Amer. Chem., Soc.*, **71**, 3078 (1949).

Intramolecular Friedel–Crafts Acylation Reaction of 4-Cycloocten-1-yl Acetyl Chloride. A Competitive [$_\pi 2_s + _\pi 2_a$] Cycloaddition

Sung Moon* and Thomas F. Kolesar

Department of Chemistry, Adelphi University, Garden City, New York 11530

Received October 11, 1973

The stannic chloride catalyzed intramolecular reaction of 4-cycloocten-1-yl acetyl chloride (**2**) yields the expected Friedel–Crafts type product, *endo*-2-chlorobicyclo[4.2.2]decan-8-one (**5**). The uncatalyzed reaction yields tricyclo[5.3.0.0^{3,10}]decan-2-one (**3**) and tricyclo[4.4.0.0^{3,10}]decan-2-one (**4**) through a [$_\pi 2_s + _\pi 2_a$] process.

The fact that a double bond can participate in an intramolecular reaction with a suitably placed cationic center has been known for a long time.[1] The first example of a solvolytic intramolecular cyclization of a simple substituted cycloalkene was reported by LeNy in 1960.[2] Since this report, many papers dealing with intramolecular participation of double bonds in cyclic systems have been published. These papers reported studies on the factors which influence ring closures,[1,3-5] aspects of the π route[6] to classical-nonclassical systems,[7,8] and synthetic routes to otherwise difficultly accessible bicyclic compounds.

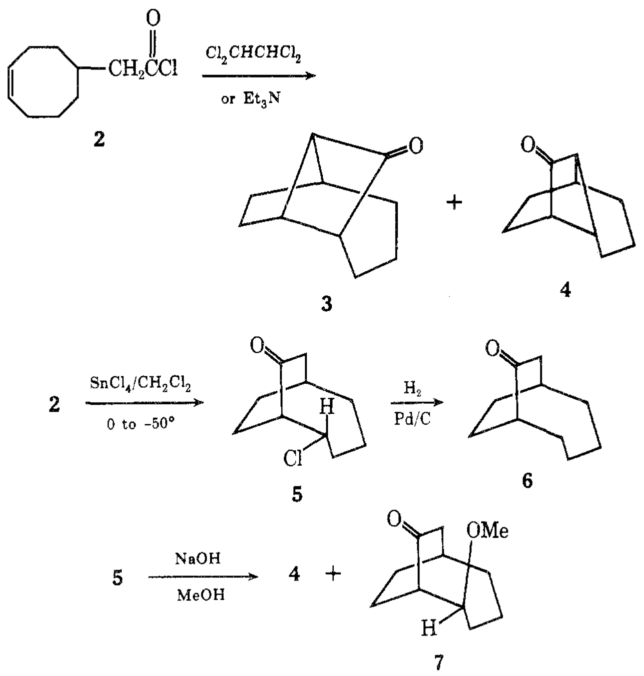
The work of Erman and Kretschmar[9] extended the study of ring closures to cases where the cationic center was derived from an acyl chloride group. A number of similar papers have appeared recently[10a,11,12] in which the Friedel–Crafts intramolecular cyclization has led to formation of bicyclic products. The Friedel–Crafts closures to give bicyclic products are of interest for two reasons. First, ring closure affords bifunctional bicyclic products having a ketone and either a halo or olefinic group, while solvolytic ring closures of sulfonate esters, etc., yield monofunctional derivatives. Second, solvolysis of esters derived from alcohols related to the acyl halide may have different selectivities. Thus, 3-(3-cyclohexen-1-yl)propionyl chloride undergoes an intramolecular ring closure,[10a] but buffered acetolysis of the tosylate of 3-(3-cyclohexen-1-yl)propyl alcohol fails to give cyclization products.[10b]

As part of a study on cationic ring closures of cyclooctenyl derivatives, we investigated the Friedel–Crafts intramolecular acylation reactions of 4-cycloocten-1-yl acetyl chloride (**2**). The stannic chloride catalyzed reaction of **2** gave products expected of a Friedel–Crafts reaction. The uncatalyzed reaction of **2** gave products which arise through the intermediacy of a ketene rather than a cationic intermediate.

Results

4-cycloocten-1-yl acetic acid (**1**) was prepared from 5-bromocyclooctene[13] by malonic ester synthesis. The acid **1** in carbon tetrachloride was converted to the acyl halide **2** with thionyl chloride. Glpc analysis of the product mixture obtained when **2** was heated at reflux in CCl_4 for 7 days showed two compounds (Scheme I) in addition to unchanged starting material. The infrared spectrum of the first unknown compound eluted, **3** (1%), showed no absorptions due to unsaturation. The carbonyl stretching frequency was unexpectedly high at 1770 cm^{-1}, indicative of a cyclobutanone ring.[14] The second unknown compound, 4 (10%), like the first, had no absorptions in the infrared spectrum which could be ascribed to an olefinic group, and also had a high carbonyl stretching frequency at 1774 cm^{-1}. The fingerprint region of both 3 and 4 showed many very sharp, moderately intense absorptions. These fingerprint absorptions suggested that the two compounds were strained.[15] The nmr spectra of both compounds confirmed the lack of an olefinic group. Finally, elemental analysis and mass spectra showed the chemical composition of 3 and 4 to be $C_{10}H_{14}O$.

Scheme I



Heating, at reflux, a solution of 2 in 1,1,2,2-tetrachloroethane for 7 days gave a higher yield of compounds 3 and 4 in the ratio of 1:10, respectively.

Structures for the $C_{10}H_{14}O$ compounds were tentatively assigned as tricyclo[5.3.0.0^{3,10}]decan-2-one (3) and tricyclo[4.4.0.0^{3,10}]decan-2-one (4). The actual assignment of structure to major and minor product depended on the chemical evidence outlined below. The two tricyclic compounds could arise by means of an intramolecular ketene cycloaddition.

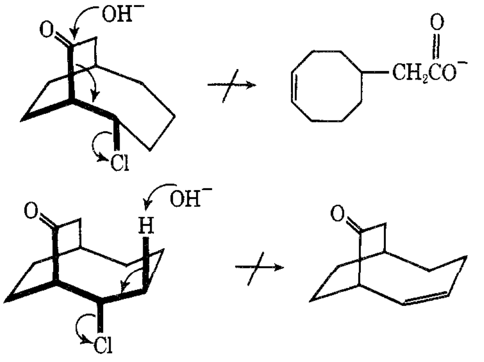
Treatment of the acyl chloride 2 with triethylamine, a standard method for the generation of ketenes,[16] produced the two tricyclodecanones in the same ratio as formed from the uncatalyzed reaction in refluxing 1,1,2,2-tetrachloroethane. The formation of the two tricyclodecanones was accompanied by the formation of dimeric products. The fact that tertiary amines catalyze the processes by which dimers and higher oligomers are formed is well known.[16]

The stannic chloride catalyzed reaction of 2 in dichloromethane at −50 to 0° gave a major product (~95%), in addition to unchanged 2 and several other unidentified products. The major component was identified as a chloro ketone 5 on the basis of its ir and nmr spectra and elemental analysis ($C_{10}H_{15}ClO$). Further, the following evidence supported the structure of the chloro ketone as *endo*-2-chlorobicyclo[4.2.2]decan-8-one (5). Hydrogenolysis[17] of the chloro ketone 5 gave bicyclo[4.2.2]decan-7-one (6)[18] as principal product (58%). In addition, the tricyclodecanone 4 (23%) and the methyl ether 7 (18%) were produced. The formation of the latter two products under the basic condition of the reaction, sodium hydroxide in methanol, is consistent with the observation below.

Since the most probable conformation of the bicyclo[4.2.2] system is not known, nmr data could not be used to assign the configuration of the chloro group. Degradation of the chloro ketone 5 with base was carried out to determine the configuration of the chlorine atom.[9,12]

Treatment of 5 with methanolic sodium hydroxide at reflux for 24 hr gave two products. The first product was identical with 4 and the second product was a methyl ether 7. The nmr spectrum of 7 is similar to that of the starting chloro ketone in the methylene envelope region, indicating that no rearrangement of the bicyclic skeleton had taken place.[19] Examination of molecular models of the bicyclo[4.2.2]decane system shows that conformations with a trans diaxial array involving the endo C-2 chlorine atom which would lead to elimination or cleavage would not be highly populated because severe transannular and 1–3 interactions were present.

It has been noted that the bicyclo[4.2.1]non-2-yl system or the carbonium ion does not readily eliminate, as compared to the isomeric bicyclo[3.3.1]non-2-yl system or its carbonium ion.[20] No explanation has been offered for this difference, but examination of models of the bicyclo[4.2.1]nonane system indicates that nonbonded interactions are important. This is shown in the dissociation constants of the cyanohydrins of the various bicyclo[4.2.1]nonanones.[21] The cyanohydrins are destabilized relative to the ketones because of severe nonbonded interactions.



The structure of the chloro ketone 5 was assigned as *endo*-2-chlorobicyclo[4.2.2]decan-8-one on the basis of the fact that the tricyclodecanone 4 must arise by an SN2 displacement of the chloro group by the enolate of the ketone, generated under the basic conditions of the reaction. There are similar examples of such transannular displacements in the literature.[22] Treatment of 1-acetyl-4-chlorocyclooctane with a variety of bases in different solvent systems affords good yields of 1-acetylbicyclo[4.2.0]octane.[22a]

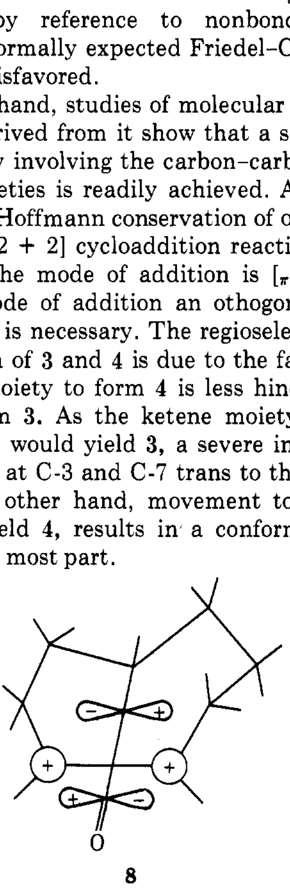
To determine if the Friedel–Crafts pathway might be competitive with the ketene intramolecular cycloaddition pathway *in the uncatalyzed reaction*, a study was performed to determine the stability of 5 to the uncatalyzed conditions. The chloro ketone 5 was heated in 1,1,2,2-tetrachloroethane at reflux. Periodically samples were withdrawn and subjected to glpc analysis. After 48 hr, 89% of 5 remained and the tricyclodecanone 4 had been formed. Formation of 4 probably arises through the reaction of the enol or enolate of 5. Because the half-life of 5 under the reaction conditions is approximately 11.5 days and no 5 is detected in the uncatalyzed reaction, one can conclude that the Friedel–Crafts pathway is not competitive to the ketene intramolecular cycloaddition.

Discussion

For ring closure or double-bond participation to be important in cationic reactions of the type studied here, two criteria must be met. First, the energy required to effect ring closure or double-bond participation must not be much greater than the energy required for any other processes by which starting material can be transformed into product(s). Second, the energy required to effect ring closure or double-bond participation must be such that the energy level is reasonably populated under the reaction conditions.

Inspection of molecular models of 2 shows that, in the conformation of closest approach, the distance between the potential cationic center and the midpoint of the double bond is 1.1 Å. The chloro group is thrust down toward the double bond, causing a serious nonbonded interaction. In uncatalyzed Friedel–Crafts reactions the reacting species is considered to be a tight ion pair;[9] so the molecular model should give a close approximation to the reacting species. In addition, a 1,5-nonbonded interaction involving the cis C-2 and C-6 hydrogen atoms is present in this conformation. Estimates of the energy involved can be obtained by reference to nonbonded interaction curves.[23] The normally expected Friedel–Crafts reaction is thus sterically disfavored.

On the other hand, studies of molecular models of 2 and the ketene 8 derived from it show that a slightly distorted orthogonal array involving the carbon–carbon double bond and ketene moieties is readily achieved. According to the Woodward and Hoffmann conservation of orbital symmetry rules, thermal [2 + 2] cycloaddition reactions are symmetry allowed if the mode of addition is $[{}_{\pi}2_s + {}_{\pi}2_a]$.[24] To achieve this mode of addition an othogonal array of the reacting species is necessary. The regioselectivity observed in the formation of 3 and 4 is due to the fact that rotation of the ketene moiety to form 4 is less hindered than that required to form 3. As the ketene moiety moves toward carbon 1, which would yield 3, a severe interaction of the hydrogen atoms at C-3 and C-7 trans to the ketene moiety occurs. On the other hand, movement toward carbon 2, which would yield 4, results in a conformation which is staggered for the most part.



8

While one would not expect reaction through a ketene or ketene-like intermediate to compete favorably with the normally expected Friedel–Crafts mode of reaction, the formation of ketenes when acyl halides are heated is well documented.[25] Although Erman and Kretschmar did not observe the formation of products arising through the intermediacy of a ketene, they suggested the possible formation of a ketene to account for rearrangements which occur in the uncatalyzed reaction of 4-cycloocten-1-yl carbonyl chloride.[9] The chemistry of ketenes, protonated ketenes, and "ketene-like" species has been the subject of recent experimental and theoretical studies.[26]

In contrast to the uncatalyzed reaction of 2, the stannic chloride catalyzed reaction proceeded through the expected Friedel–Crafts reaction. Inspection of molecular models shows that closure to bicyclo[4.2.2]decane products is favored over closure to bicyclo[3.3.2]decane products because of steric hindrance. The reason(s) for the stereospecificity observed in the formation of the endo isomer of 5 is difficult to define. It is known that the products obtained are dependent on the structure of the reactant(s), polarity of the solvent, catalyst, and temperature.[9] Thus, when freshly sublimed aluminum chloride is used as catalyst in the reaction of *cis*-cyclooctene and acetyl chloride the predominant product is 4-acetyl-1-ethylcyclohexene. However, if the sublimed catalyst is deactivated by exposure to the atmosphere, 1-acetyl-4-chlorocyclooctane is the main product.[22a] The catalyst exerts its effect in two ways. First, the size of the catalyst–substrate complex will affect the cis–trans product ratio. Second, a more active catalyst will increase the lifetime of the carbonium ions formed and promote rearrangements.[9] Molecular models of bicyclo[4.2.2]decan-7-one indicate that both the exo and endo sides of the system at the 2 carbon are amenable to nucleophilic attack. The presence of a fairly large complex as would be formed with stannic chloride and the carbonyl function may present enough hindrance to cis attack giving the exo product and thus the trans endo product 5 is formed. Fickes and Kemp also observed the intramolecular stereospecific trans addition of cyclohept-4-ene-1-carbonyl chloride in the presence of aluminum chloride and suggested the possible intervention of a nonclassical intermediate.[12]

Experimental Section

Nmr spectra were determined on a Varian A-60 spectrophotometer, using tetramethylsilane as an internal standard. Ir spectra were determined on a Perkin-Elmer 257 grating infrared spectrophotometer using polystyrene film as the calibration standard. Solution ir spectra were recorded at concentrations of 5–10%. Boiling points and melting points are uncorrected. Melting points were determined on a Thomas-Hoover 6406-H apparatus. Glpc separations were performed on an F & M Scientific 720 dual column programmed temperature gas chromatograph. A 2 ft × 0.25 in. column packed with 20% neopentyl glycol succinate on 60/80 mesh Chromosorb W acid washed and treated with hexamethyldisilane was used.

4-Cycloocten-1-ylacetic Acid (1). A 1-l. flask equipped with a dropping funnel and a water condenser protected with a calcium chloride drying tube was charged with 12.5 g (0.500 g-atom) of sodium in small pieces. Anhydrous ethanol (200 ml) was added, and the mixture was stirred by means of a magnetic stirrer. When the initial reaction had subsided, an additional 300 ml of anhydrous ethanol was added over 0.5 hr.The mixture was heated on the steam bath at reflux until all the sodium had reacted. The solution was allowed to cool to approximately 40° and 80.0 g (0.500 mol) of diethyl malonate was added over 15 min. To the stirred solution was added 94.6 g (0.500 mol) of 4-cycloocten-1-yl bromide. The mixture was heated at reflux for 72 hr. The condenser was replaced with a simple distilling head and the mixture was heated on the steam bath until no more alcohol distilled. To the concentrate was added 40 g (1.0 mol) of sodium hydroxide dissolved in 150 ml of water. The mixture was heated at reflux for 18 hr. The solution was allowed to cool to room temperature and acidified with HCl. The solution was filtered and the crude 4-cycloocten-1-ylmalonic acid was air dried. The crude malonic acid (65 g, 61%) was placed in a 250-ml round-bottomed flask and distilled with decarboxylation. The acid 1 was collected as a viscous oil (46 g, 55% overall). Portions of the oil were crystallized from a hexane solution at Dry Ice–acetone temperature. The first crop of crystals was recrystallized twice to give the analytical sample, mp 34.2–35.5°. The acid had the following properties: ir (CCl_4) 3400–3050 (COOH), 3010 (C=CH), 1700 cm^{-1} (C=O); nmr (CCl_4) τ −0.10 (s, 1, COOH), 4.44 (m, 2, C=CH), 7.2–9.2 (complex with major absorptions at 7.82 and 8.49, 13, other hydrogens).

Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.28; H, 9.77.

Uncatalyzed Reaction of Acyl Chloride 2. A. In Carbon Tetrachloride. To a solution of 12.2 g (73.0 mmol) of 1 in 30 ml of carbon tetrachloride was added 8.7 g (73 mmol) of thionyl chloride. The solution was heated at reflux for 1 hr and concentrated and an ir spectrum (film) was taken, C=O 1800 cm^{-1}. A solution of 5.0 g of the acyl chloride **2** in 50 ml of carbon tetrachloride was heated at reflux for 7 days. To the refluxing solution was added 20 ml of water and the mixture was heated at reflux for 1 hr. The organic layer was separated and the aqueous layer was extracted with carbon tetrachloride. The combined extracts were dried and glpc analysis was performed at 160°. The product composition by area was **3**, 1%; **4**, 10%; and **2**, 89%. The products had the following properties.

3 had mp 40–42°, as collected from glpc; ir (CS_2) 2920, 2870, 2840, 1770, 1355, 1308, 1298, 1242, 1216, 1156, 1132, 1028, 992, 936, and 896 cm^{-1}, the bands in the fingerprint region were moderately intense and sharp, characteristic of small strained rings; nmr (CCl_4) τ 6.54, (m, 1, bridgehead α to carbonyl), 6,74 (m, 1, bridgehead α to carbonyl), 7.0–9.0 (complex with major absorptions at 7.10, 7.24, 7.34, 7.50, 7.90, 8.34, 8.44, 8.54, and 8.60, 12 H); mass spectrum (75 eV) *m/e* 150, 122 (−CO).

Anal. Calcd for $C_{10}H_{14}O$: C, 79.96; H, 9.39. Found: C, 79.81; H, 9.14.

4 had mp 152–156° (sealed tube), after collection from glpc and sublimation at 135° (15 mm); ir (CS_2) 2932, 2874, 2850, 1774, 1375, 1340, 1308, 1282, 1274, 1250, 1232, 1188, 1158, 1131, 1108, 1054, 1028, 986, 958, 932, 901, and 862 cm^{-1}, the bands in the fingerprint region were moderate to weak in intensity and sharp, characteristic of small strained rings; nmr (CCl_4) τ 6.42 (m, 1, bridgehead α to carbonyl), 7.0–9.0 (complex with major absorptions at 7.08, 7.17, 7.28, 7.35, 7.50, 7.56, 8.03, and 8.28, 13 H); mass spectrum (75 eV) *m/e* 150, 122 (−CO).

Anal. Calcd for $C_{10}H_{14}O$: C 79.96; H 9.39. Found: C, 79.85; H, 9.20.

B. In 1,1,2,2-Tetrachloroethane. The acyl chloride **2** prepared from 1.68 g of **1**, as above, was dissolved in 10 ml of tetrachloroethane and the solution was heated at reflux for 7 days. A crystalline product had formed on the condenser. The solution was concentrated on a rotary evaporator and the residue was sublimed at 130° and water aspirator pressure. An off-white solid, 750 mg, was collected. The solid consisted of **3** and **4** in a ratio of 1:10, respectively (glpc analysis). The residue consisted of unchanged **2** and some **3** and **4**.

Stannic Chloride Catalyzed Reaction of 2. The acyl chloride **2** prepared from 1.68 g of **1** as above was dissolved in 30 ml of dichloromethane. The solution was cooled to −50° in a Dry Ice–acetone bath and 2.60 g (10.0 mmol) of stannic chloride (1:1 reactant/catalyst mole ratio) was added over 5 min. The solution was kept at −50° for 0.5 hr and then removed from the bath. When the temperature of the solution reached 0°, a mixture of ice and water was added to quench the reaction. The dichloromethane layer was drawn off and the aqueous layer was extracted with one 10-ml portion of dichloromethane. The combined dichloromethane solutions were dried ($MgSO_4$) and concentrated. Analysis by glpc (area integration) at 160° showed **2**, 3%; **5**, 95%; and two unidentified peaks, 2%. The chloro ketone **5** had the following properties: mp 48–52°, as collected from glpc; ir (CS_2) 2920, 2880, 1705, 1335, 1325, 1290, 1235, 1160, 1115, 1035, 964, 935, 830, and 785 cm^{-1}; nmr (CCl_4) τ 5.5–5.9 (m, 1, ClCH), 7.2–9.3 (complex with major absorptions at 7.35, 7.58, 7.65, 7.86, 8.03, 8.05, and 8.27, 14, other hydrogens).

Anal. Calcd for $C_{10}H_{15}ClO$: C, 64.34; H, 8.10. Found: C, 64.60; H, 8.17.

Hydrogenolysis of 5. To 10 ml of methanol was added 107 mg of **5**, 90 mg of 5% palladium on carbon, and 120 mg of potassium hydroxide. The mixture was hydrogenated at 30 psi for 4.5 hr in a Parr low-pressure hydrogenation apparatus. The solution was filtered and allowed to concentrate overnight by evaporation. The solution was further concentrated on a rotary evaporator to give a mixture of inorganic and organic products. The mixture was extracted with petroleum ether (bp 30–60°) and glpc analysis and separations were performed. The following temperature program was used: isothermal at 135° until **6** eluted and then at 5°/min to 160°. The ir spectrum of the major product **6** was identical with that of an ir spectrum of an authentic sample[17] of bicyclo[4.2.2]decan-7-one (**6**). The two other products identified were **4** (23%) and **7** (18%). A fourth compound (1%) was unidentified.

Treatment of 5 with 10% Methanolic Sodium Hydroxide Solution. To 30 ml of a 10% methanolic sodium hydroxide solution was added 252 mg of **5**. The solution was heated at reflux for 24 hr and cooled. The solution was diluted with 50 ml of water and extracted with three 25-ml portions of ether. The combined extract was washed with three 10-ml portions of water and dried ($MgSO_4$), and glpc analysis was performed at 160°. Two compounds eluted. The minor component (16%, area integration) was identical with **4** (ir and nmr spectra). The major product (84%) was the methyl ether **7**: ir (CS_2) 2975, 2930, 2910, 2872, 2820, 1700, 1407, 1337, 1285, 1238, 1185, 1146, 1095, 1038, 929 cm^{-1}; nmr (CCl_4) τ 6.70 (s, 3, CH_3O), this peak is superimposed over an absorption at 6.5–6.7 (m, OCH), other absorptions at 7.28, 7.40, 7.65, 7.98, 8.15, 8.22, 8.40, and 8.60 (14, other hydrogens).

Anal. Calcd for $C_{11}H_{18}O$: C, 72.51; H, 9.95. Found: C, 72.47; H, 9.84.

Stability of 5 under Uncatalyzed Conditions. A solution of 20 mg of **5** in 10 ml of 1,1,2,2-tetrachloroethane was heated at reflux. After 24 hr at reflux a sample was withdrawn and analyzed by glpc. The relative areas found were 95% **5** and 5% **4**. After 48 hr at reflux the ratios were 89% **5** and 11% **4**.

Treatment of Acyl Halide 2 with Triethylamine. To a solution of 1.86 g of **2** in 25 ml of ether cooled in an ice-water bath was added dropwise 1.01 g (10 mmol) of triethylamine. The solution was swirled after each addition; a white precipitate formed immediately. The mixture was allowed to warm to room temperature, extracted with dilute HCl, dried ($MgSO_4$), and analyzed by glpc. The chromatogram showed the tricyclodecanones **3** and **4** in the ratio of 1:10, respectively, identified by ir. In addition a number of dimeric products at longer retention times were observed. From total area integration the yield of monomeric products was calculated as 45%.

Registry No.—1, 50585-13-2; **2,** 50585-14-3; **3,** 50585-15-4; **4,** 50585-16-5; **5,** 50585-25-6; **7,** 50585-26-7; diethyl malonate, 105-53-3; 4-cycloocten-1-yl bromide, 4103-12-2; $SnCl_4$, 7646-78-8.

References and Notes

(1) For leading references see P. D. Bartlett, S. Bank, R. J. Crawford, and G. H. Schmid, *J. Amer. Chem. Soc.*, **87**, 1288 (1965).

(2) G. LeNy, *C. R. Acad. Sci.*, **251**, 1526 (1960).

(3) P. D. Bartlett and G. D. Sargent, *J. Amer. Chem. Soc.*, **87**, 1297 (1965).

(4) P. D. Bartlett, W. S. Trahanovsky, D. A. Bolon, and G. H. Schmid, *J. Amer. Chem. Soc.*, **87**, 1314 (1965).

(5) E. N. Marvel, D. Sturmer, and R. S. Knutson, *J. Org. Chem.*, **33**, 2991 (1968).

(6) S. Winstein and P. Carter, *J. Amer. Chem. Soc.*, **83**, 4485 (1961).

(7) H. L. Goering and M. F. Sloan, *J. Amer. Chem. Soc.*, **83**, 1397 (1961).

(8) H. M. Walborsky, M. E. Baum, and A. A. Youssef, *J. Amer. Chem. Soc.*, **83**, 988 (1961).

(9) W. F. Erman and H. C. Kretschmar, *J. Org. Chem.*, **33**, 1545 (1968).

(10) (a) E. N. Marvell, G. J. Gleicher, D. Sturmer, and K. Salisbury, *J. Org. Chem.*, **33**, 3393 (1968); (b) E. N. Marvell, R. S. Knutson, T. McEwen, D. Sturmer, W. Federici, and K. Salisbury, *ibid.*, **35**, 391 (1970).

(11) R. L. Cargill and A. M. Foster, *J. Org. Chem.*, **35**, 1971 (1970).

(12) G. N. Fickes and K. C. Kemp, *Chem. Commun.*, **84** (1973).

(13) K. Ziegler and H. Wilms, *Justus Liebigs Ann. Chem.*, **567**, 1 (1950).

(14) R. M. Silverstein and G. C. Bassler, "Spectrometric Identification of Organic Compounds," 2nd ed, Wiley, New York, N. Y., p 88.

(15) M. Hanack, H. Schneider-Bernlohr, H.-J. Schneider, R. Huttinger, and G. Wentrup, *Justus Liebigs Ann. Chem.*, **717**, 41 (1968).

(16) W. E. Handford and J. C. Sauer, *Org. React.*, **3**, 108, 124 (1966); S. W. Baldwin and E. H. Page, Jr., *J. Chem. Soc., Chem. Commun.* 1337 (1972); N. Lacey in "The Chemistry of Alkenes," S. Patai, Ed., Interscience, New York, N. Y., 1964, pp 1168–1169.

(17) M. G. Reinecke, *J. Org. Chem.*, **29**, 299 (1964).

(18) We wish to thank Professor Maitland Jones, Jr., for an ir spectrum of bicyclo[4.2.2]nonan-7-one: M. Jones, Jr., S. D. Reich, and L. T. Scott, *J. Amer. Chem. Soc.*, **92**, 3118 (1970).

(19) We have observed that the methylene envelope region of the nmr spectrum of bicyclic compounds has distinctive characteristics. The derivatives of the bicyclo[3.3.2]decane system show a similar nmr spectrum in the methylene envelope region which is decidedly different from spectra of bicyclo[4.2.2]decane derivatives.

(20) K. H. Baggaley, J. R. Dixon, J. M. Evans, and S. H. Graham, *Tetrahedron*, **23**, 299 (1967).

(21) M. Hartmann, *Justus Liebigs Ann. Chem.*, **724**, 102 (1969).

(22) (a) J. K. Groves and N. Jones, *J. Chem. Soc. C*, 2350 (1969); (b) N. Dufort and J. Lafontaine, *Can. J. Chem.*, **46**, 1065 (1968); (c) N. A. Nelson and G. A. Mortimer, *J. Org. Chem.*, **22**, 1146 (1957).

(23) D. E. Williams, *J. Chem. Phys.*, **45**, 3770 (1966).

(24) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970, pp 65–73; R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969). For examples see A. Hassner, V. R. Fletcher, and D. P. G. Hamon, *J. Amer. Chem. Soc.*, **93**, 264 (1971); W. T. Brady and E. F. Hoff, Jr., *J. Org. Chem.*, **35**, 3733 (1970).

(25) M. S. Newman, A. Arkell, and T. Fukunaga, *J. Amer. Chem. Soc.*, **82**, 2498 (1960).

(26) A. C. Hopkinson, *J. Chem. Soc., Perkin Trans. 2*, 795 (1973); G. A. Olah and P. W. Westerman, *J. Amer. Chem. Soc.*, **95**, 3706 (1973).