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Synthesis of Medium-Ring Cycloalkene-1-carboxylic Acids and Thermodynamic Properties of the Cycloundecene-1-carboxylic Acid System[1]

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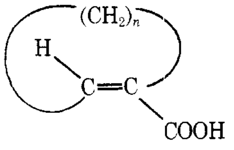
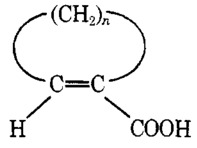
Cyclononene-1-carboxylic acid (*E* isomer), (*E*)-cyclodecene-1-carboxylic acid, (*E*)- and (*Z*)-cycloundecene-1-carboxylic acid, and (*E*)- and (*Z*)-cyclododecene-1-carboxylic acid were synthesized by aqueous alkaline hydrolysis of the corresponding 4-chloro-3,4-poly(methylene)-2-pyrazolin-5-ones. The stereochemistry of the *E*/*Z* acid pairs formed was determined by NMR data and showed the *Z* isomer as the predominant product. The standard free energies, enthalpies, and entropies of isomerization for the*E*/*Z* cycloundecene-1-carboxylic acids (acetic acid anhydrides) were determined at various temperatures using an acetic anhydride–triethylamine mixture as an isomerization medium. The thermodynamic data showed that the (*E*)-cycloundecene-1-carboxylic acid product is the more stable isomer.

Previous studies[2–5] have demonstrated the generality of the conversion of aryl and alkyl 4-halo-3,4-disubstituted-2-pyrazolin-5-ones to the acyclic trisubstituted α,β-unsaturated carboxylic acids. This method of preparation represents a useful synthetic route to acids difficult to obtain by other methods in that the labile acyclic (*Z*)-α,β-alkenoic acid is formed in predominant amounts in both the alkyl and aryl series. In the cyclic series, the *E* isomer was the *exclusive* product formed for cyclohexene through cyclooctene-1-carboxylic acid.[6] The object of this investigation is to determine if this method is applicable to the synthesis of medium-ring (*Z*)-cycloalkene-1-carboxylic acids **1** and, if a mixture of acids is formed, to determine at least in one case their relative stabilities. General methods for the preparation of (*E*)- and (*Z*)-cycloalkene-1-carboxylic acids **1** and **2** have not been readily available.[7] The cycloalkene-1-carboxylic acids that have been prepared are of interest to others because their salts have shown to be very powerful cholertics and these compounds have been used in the treatment of heptovascular conditions and hepatic insufficiency.[7] The methyl and ethyl esters of these acids are pleasant smelling and are of interest to the cosmetic industry as additives.[7]



1

Z isomer



2

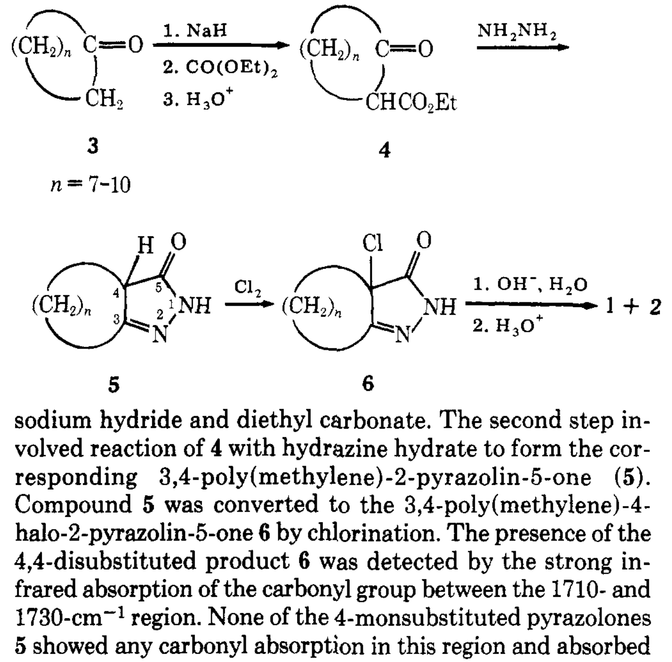
E isomer

n = 7–10

Accordingly, an attempt was made to synthesize the (*E*)- and (*Z*)-cycloalkene-1-carboxylic acids and, for purposes of clarity, the overall synthetic route is shown.

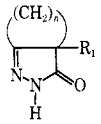
The first step in the synthesis (Scheme I) involved the conversion of the cycloalkanone **3** to the respective β-keto ester **4**, which was readily accomplished by reaction of **3** with sodium hydride and diethyl carbonate. The second step involved reaction of **4** with hydrazine hydrate to form the corresponding 3,4-poly(methylene)-2-pyrazolin-5-one (**5**). Compound **5** was converted to the 3,4-poly(methylene)-4-halo-2-pyrazolin-5-one **6** by chlorination. The presence of the 4,4-disubstituted product **6** was detected by the strong infrared absorption of the carbonyl group between the 1710- and 1730-cm^{-1} region. None of the 4-monsubstituted pyrazolones **5** showed any carbonyl absorption in this region and absorbed at lower frequencies, probably due to the C-4 hydrogens being involved in the corresponding tautomeric enol forms of **5**. These data are summarized in Table I. The final reaction involved treatment of the resultant 4-chloropyrazolone with dilute aqueous alkali followed by acifidication.

Scheme I



In the cases of cyclononene- and cyclodecene-1-carboxylic acids, only the *E* isomers **2** were formed. For the cycloundecene-1-carboxylic acids a *Z*/*E* isomer ratio of 3:1 was obtained, while the cyclododecene-1-carboxylic acids were formed in a 4:1 *Z*/*E* ratio. The quantitative determination of acids was readily accomplished using proton magnetic resonance. In an analysis of a mixture of *E* and *Z* isomers utilizing proton magnetic resonance, the vinyl proton peaks were well separated and the relative areas under these peaks were propor-

Table I. Carbonyl IR Absorptions of Pyrazolones



Compd	Registry no.	R_1	IR ($\gamma_{C=O}$), cm^{-1}
5 (n = 7)	63657-92-1	H	1620
5 (n = 8)	63657-99-8	H	1590
5 (n = 9)	63658-00-4	H	1615
5 (n = 10)	63658-01-5	H	1600
6 (n = 7)	63658-02-6	Cl	1725
6 (n = 8)	63658-03-7	Cl	1730
6 (n = 9)	63658-04-8	Cl	1725
6 (n = 10)	60848-29-5	Cl	1710

Table II. Thermodynamic Data for the Cycloundecene-1-carboxylic Acid Isomerization System [a]

T, K	Av K,[a] E/Z	$\Delta G°$,[b] kcal/mol	$\Delta H°$,[c] kcal/mol	$\Delta S°$, cal/mol K
355.1 ± 0.5	34.1	-2.4_9	-7.2_7	−13.5
343.1 ± 0.5	45.1	-2.6_0	-7.2_7	−13.6
334.0 ± 0.5	53.6	-2.6_4	-7.2_7	−13.9
323.2 ± 0.5	94.8	-2.9_3	-7.2_7	−13.4

[a] Each value represents the mean of ten determinations. [b] Maximum percent error for $\Delta G°$ was calculated[15] by taking the maximum differences in the equilibrium constants of the ten runs. The maximum percent error at the highest temperature was 1.96 to 4.55% at the lowest temperature. [c] A least-squares fit for these van't Hoff plots gave a correlation coefficient of 0.9781.

tional to the ratio of components. The relative positions of the resonance lines of the vinyl proton were also characteristic of its stereochemistry; the shielding value of the single proton in the E isomer was consistently higher[5,8] in δ units than that of the corresponding Z isomer by about 0.7 ppm. This same trend in chemical shift of the vinyl protons was also observed by other workers in cycloalk-2-en-1-ones,[9] 3-methoxycarbonylcycloalkenones,[10] and *cis*- and *trans*-cyclodec-2-enones.[11] In planar cycloalk-2-en-1-one systems with efficient conjugation between the double bond and carbonyl group, the C-3 proton is strongly deshielded relative to the C-2 proton by mesomeric electron withdrawal.[9] With respect to the cis and trans systems, the 3-H resonance for *cis*-cyclodec-2-enone actually appears 0.57 ppm to higher field than that due to the 2-H, which illustrates this ketone's lack of conjugation. In contrast, for the trans ketone the 3-H signal is at 0.32 ppm to lower field than the 2-H.[11]

Cope[12] has shown that in the case of nine- and ten-carbon cycloalkenes the Z isomer has the greater thermodynamic stability, while the inverse is true for the 11- and 12-carbon cycloalkenes. Consequently, it was of interest to determine the effect a carboxylic acid derivative has on the thermodynamic stability of these rings. As cycloundecene is the crossover point between E- and Z-ring stabilities, the cycloundecene-1-carboxylic acids were chosen as the model system. The equilibration reaction was effected by using a mixture of equal amounts of acetic anhydride and triethylamine.[13,14] The equilibrated acids were extracted out of the isomerization medium using a slightly modified procedure developed by Zimmerman.[13] Percent recoveries for this extraction method did not vary with E/Z isomer ratios, and it is apparent that both isomers were extracted to the same extent. The acids were methylated with diazomethane, and the corresponding methyl esters were subjected to gas chromatographic analysis. Analysis of known E/Z isomer mixtures showed no effect on the isomeric ratio due to gas chromatographic conditions. The thermodynamic data for the cycloudecene-1-carboxylic acid isomerization system is summarized in Table II.

The apparent equilibrium constants are related to the actual thermodynamic equilibrium constants K, through the following relationship

$$(\gamma_E/\gamma_Z)K' = K$$

where γ_E/γ_Z is the ratio of activity coefficients. At the total concentrations of (E)- and (Z)-cycloundecene-1-carboxylic acids studies (molarity ≤0.17, mole fraction ≤0.018), it is reasonable to assume that the activity coefficients are very close to unity. Moreover, for such closely related substances as the (E)- and (Z)-acid isomers, the ratios of activity coefficients would most likely be 1 and thus $K = K'$.

As a convention, the values reported in Table II are for the isomerization of the Z isomer (trans ring) to the E isomer (cis ring). On comparison with cycloundecene isomer pairs,[12] it is apparent that the trans ring (E isomer) is more thermodynamically stable in the unsubstituted case, while the cis ring (E isomer) is the more stable when the carboxylic acid derivative is introduced.

The electron-transfer absorption in the ultraviolet of (E)- and (Z)-cycloundecene-1-carboxylic acids showed the E isomer with a slightly shorter wavelength and significantly higher absorption intensity than the Z isomer. Murrell[16] has suggested that for the electronic excitation of a conjugated molecule to a state of predominantly electron-transfer character, steric distortion should result either in no shift or in a small bathochromic shift compared to the planar system. Braude and Sondheimer[17] have shown that the angles of noncoplanarity can be estimated from the relationship, $\epsilon/\epsilon_0 = \cos^2\theta$, where ϵ is the molar absorbancy of the sterically hindered compound and ϵ_0 that of a planar reference analogue. Assuming that the carboxy group in the E isomer is coplanar with the double bond, based on the relative molar absorbancy indices, the Z isomer is twisted approximately 38° from planarity. The higher shielding value in δ units for the vinyl proton of the E isomer also gave support that this isomer is effectively more conjugated than the corresponding Z isomer. Effective electron delocalization requires proper coplanar orientation of the two ring carbons and the exocyclic carbonyl group of the acid. Presumably, the increased steric interactions in the Z isomer accounts for its decreased conjugation and lower stability. It is apparent that this change in stability is brought about by changes in both $\Delta H°$ and $\Delta S°$. For cycloundecene,[12] $\Delta H°$ was slightly positive (0.12 kcal/mol) and $\Delta S°$ negative (−1.5 cal/mol K). In the corresponding carboxylated ring systems, $\Delta H°$ was negative (−7.27 kcal/mol) and $\Delta S°$ was more negative (−13.4 to −13.9 cal/mol K).

Thus, it appears that the driving force[2,18] favoring the labile isomer of a geometric pair of α,β-olefinic acids in the treatment of cyclic 3,4-disubstituted 4-halopyrazolones with aqueous sodium hydroxide is not sufficient to overcome the natural reluctance of a 1-substituted cyclononene[19] or cyclodecene[11,19] to support the trans ring, while in the cycloundecene-1-carboxylic acid case the less stable Z acid (trans ring system) was formed in predominant amount. The extensions of this method to the possible synthesis of larger ring unknown (Z)-cycloalkene-1-carboxylic acids and investigation of their thermodynamic properties are anticipated.

Experimental Section

All melting and boiling points are uncorrected. IR spectra were determined with a Perkin-Elmer Model 621 double-beam spectrophotometer and were calibrated vs. polystyrene. NMR spectra were recorded on a Perkin-Elmer 60-MHz R20A spectrometer with tetramethylsilane as an internal standard. Ultraviolet spectra were obtained on a Cary 14R recording spectrometer. VPC analyses were performed with a Perkin-Elmer 900 gas chromatograph (thermal-conductivity detector). Analyses were done by Galbraith Laboratories, Inc., Knoxville, Tenn. 37921.

2-Carbethoxycycloalkanones, 4 (*n* = 7–10). The method of Rhoads[20] et al. involving carbethoxylation by diethyl carbonate and sodium hydride was used in the preparation of 2-carbethoxycyclononane (75%), 2-carbethoxycyclodecanone (65%), 2-carbethoxycycloundecanone (65%), and 2-carbethoxycyclododecanone (70%). **3** (*n* = 10) was also prepared by the method of Shahak[21] involving carbethoxylation by triethyl phosphonoformate–sodium hydride in 65% average yield.

3,4-Poly(methylene)-2-pyrazolin-5-ones, 5 (*n* = 7–10). An ice-cooled, stirred solution of 4 in ethanol was treated slowly with a solution of 95% hydrazine in ethanol. Equimolar amounts of 4 and 95% hydrazine were used. After each addition of hydrazine, the reaction mixture was allowed to cool, as the reaction was exothermic. Addition took about 10–12 min, and the solution was stored in the freezer overnight. A white crystalline solid formed, was filtered by suction, and washed three times with ice-cold ethanol. Recrystallization from ethanol yielded **5** (*n* = 7) as white plates in 90% average yield: mp 235–236°C; IR (KBr) 3110 (sh), 2950 (br), 1620 cm^{-1}; NMR (pyridine) δ 1.2–2.8 (complex m, 15 H, $-(CH_2)_7-$ and C-4 H), 10.15 (s, 1 H, N-H); UV (95% ethanol) λ_{max} 251 nm (log ϵ 3.93).

Anal. Calcd for $C_{10}H_{16}N_2O$: C, 66.64; H, 8.95; N, 15.53. Found: C, 66.43; H, 9.22; N, 15.41.

5 (*n* = 8) as white plates in 95% average yields: mp 220–221 °C; IR (KBr) 3020 (sh), 2850 (br), 1590 cm^{-1}; NMR (pyridine) δ 1.0–2.9 (complex m, 17 H, $-(CH_2)_8-$ and C-4 H), 10.15 (s, 1 H, N-H); UV (95% ethanol) λ_{max} 251 nm (log ϵ 3.77).

Anal. Calcd for $C_{11}H_{18}N_2O$: C, 68.00; H, 9.34; N, 14.41. Found: C, 67.73; H, 9.12; N, 14.40.

5 (*n* = 9) as white plates in 95% average yields: mp 184–185 °C; IR (KBr) 3210 (sh), 2840 (br), 1615 cm^{-1}; NMR (pyridine) δ 0.7–3.0 (complex m, 19 H, $-(CH_2)_9-$ and C-4 H), 10.30 (s, 1 H, N-H); UV (95% ethanol) λ_{max} 253 nm (log ϵ 3.98).

Anal. Calcd for $C_{12}H_{20}N_2O$: C, 69.23; H, 9.61; N, 13.46. Found: C, 69.46; H, 9.86; N, 13.18.

5 (*n* = 10) as a white solid in 92% average yields: mp 202–203 °C; IR (KBr) 3110 (sh), 2850 (br), 1600 cm^{-1}; NMR (pyridine) δ 0.4–2.5 (complex m, 21 H, $-(CH_2)_{10}-$, and C-4 H), 11.6 (s, 1 H, N-H); UV (95% ethanol) λ_{max} 251 nm (log ϵ 3.84).

Anal. Calcd for $C_{13}H_{22}N_2O$: C, 70.23; H, 9.97; N, 12.60. Found: C, 70.04; H, 10.06; N, 12.56.

3,4-Poly(methylene)-4-chloro-2-pyrazolin-5-ones, 6 (*n* = 7–10). A 100-mL three-neck flask fitted with a condenser, magnetic stirrer, and gas inlet tube was charged with 0.1–0.02 mol of **5** and 40 mL of CH_2Cl_2. With rapid magnetic stirring, Cl_2 gas was introduced below the surface of the suspension at ambient temperature until the mixture became homogeneous (usually in about 5 min) and a mild exothermic reaction and concomitant yellow color were observed. After about 4 h, evolution of HCl ceased and the solvent was evaporated with the aid of a rotatory evaporator, yielding a colorless solid. For analytical purposes, **6** (*n* = 7–9) was recrystallized from benzene–ligroin and **6** (*n* = 10) from benzene.

6 (*n* = 7) as white plates in 71% average yields: mp 168–169 °C; IR (KBr) 3250, 2980, 1725 cm^{-1}; NMR ($CDCl_3$) δ 1.3–2.8 (complex m, 14 H, $-(CH_2)_7-$), 10.0 (s, 1 H, N-H); UV (95% ethanol) λ_{max} 269 nm (log ϵ 3.49).

Anal. Calcd for $C_{10}H_{15}N_2OCl$: C, 55.95; H, 6.99; N. 13.06; Cl, 16.53. Found: C, 55.93; H, 7.01; N, 13.00; Cl, 16.70.

6 (*n* = 8) as white plates in 69% average yields: mp 146–147 °C; IR (KBr) 3280, 2990, 1730 cm^{-1}; NMR ($CDCl_3$) δ 1.0–2.95 (complex m, 16 H, $-(CH_2)_8-$, 10.0 (s, 1 H, N-H); UV (95% ethanol) λ_{max} 269 nm (log ϵ 3.36).

Anal. Calcd for $C_{11}H_{17}N_2OCl$: C, 57.78; H, 7.44; N, 12.26; Cl, 15.52. Found: C, 57.60; H, 7.35; N, 12.21; Cl, 15.40.

6 (*n* = 9) as white plates in 77% average yields: mp 146–147 °C; IR (KBr) 3290, 2990, 1725 cm^{-1}; NMR ($CDCl_3$) δ 0.8–1.85 (complex m, 18 H, $-(CH_2)_9-$), 9.0 (s, 1 H, N-H); UV (95% ethanol) λ_{max} 268 nm (log ϵ 3.56).

Anal. Calcd for $C_{12}H_{19}N_2OCl$: C, 59.39; H, 7.84; N, 11.55; Cl, 14.62. Found: C, 59.27; H, 7.92; N, 11.44; Cl, 14.34.

6 (*n* = 10) as white plates in 75% average yields: mp 155–156 °C; IR (KBr) 3210, 2950, 1710 cm^{-1}; NMR ($CDCl_3$) δ 0.3–2.7 (complex m, 20 H, $-(CH_2)_{10}-$), 9.38 (s, 1 H, N-H); UV (95% ethanol) λ_{max} 251 nm (log ϵ 3.69).

Anal. Calcd for $C_{13}H_{21}N_2OCl$: C, 60.83; H, 8.19; N, 10.92; Cl, 13.82. Found: C, 60.79; H, 8.17; N, 10.80; Cl, 13.91.

(*E*)- and (*Z*)-Cycloalkene-1-carboxylic Acids 1 and 2. To a magnetically stirred, ice-cold 2 N sodium hydroxide solution (50 mL) cooled in an ice bath at 0–5 °C, 0.009 mol of **6** (*n* = 7–10) was added. The solid dissolved, giving the solution a yellow color with gas evolution. After gas evolution had subsided (about 3 h), stirring was continued for another 2 h in the cold at 0–5 °C, the ice bath was removed, and the stirring continued for an additional 2 h. The solution was acidified with 6 N HCl to a congo red end point (pH 3.1). The resulting solid was taken up with two 25-mL portions of ether. The combined ether extracts were extracted two times with 25 mL of $NaHCO_3$, and the bicarbonate extracts were acidified to give a yellow-white solid. The solid was extracted with ether (50 mL), dried over $MgSO_4$, and filtered, and the ether was removed.

(*E*)-Cyclononene-1-carboxylic acid, **2** (*n* = 7), was obtained in 67% average yields, mp 77–78 °C (pentane), lit.[22] mp 77–78 °C. No *Z* isomer **1** (*n* = 7) was observed.

(*E*)-Cyclodecene-1-carboxylic acid, **2** (*n* = 8), was obtained in 60% average yields, mp 128–130 °C (pentane), lit.[23] 130–131 °C. No *Z* isomer **1** (*n* = 8) was observed.

A mixture in 57% average yields was obtained of (*Z*)- and (*E*)-cycloundecene-1-carboxylic acids, 1 and **2** (*n* = 9), mp 128–135 °C (pentane). Percentages of each isomer were determined by both ^{1}H NMR and VPC (methyl esters) and gave an average 3:1 *Z*/*E* isomer ratio. No isomerization of the esters occurred under the conditions of gas chromatography (typical conditions given in equilibrium section). The ^{1}H NMR peak, due to the vinyl proton, appeared in all cases as triplets, and the values of all acid isomers studied are reported for the center of each triplet expressed in ppm and follow: *E* isomer (*n* = 7) δ 6.98 ($CDCl_3$); *E* isomer (*n* = 8) δ 6.94 ($CDCl_3$); *E* isomer (*n* = 9) δ 7.01 ($CDCl_3$); *Z* isomer (*n* = 9) δ 6.23 ($CDCl_3$); *E* isomer (*n* = 10) δ 6.85 ($CDCl_3$); *Z* isomer (*n* = 10) δ 6.18 ($CDCl_3$).

The mixture of *Z*/*E* acids 1 and **2** (*n* = 9) was separated by a fractional extraction method previously described.[2] Separation was obtained at fractions 7 and 8: mp of E isomer 116–117°C, lit.[7] 116–117 °C; UV λ_{max} (95% EtOH) 219.5 nm (ϵ 12 950); *Z* isomer 136–138 °C, lit. 138–139 °C;[7] UV λ_{max} (95% EtOH) 222 nm (ϵ 7930).

A mixture in 52% average yields was obtained of (*Z*)- and (*E*)-cyclododecene-1-carboxylic acids, **1** and **2** (*n* = 10), mp 120–123°C (lit.[7] mp of mixture 121–125 °C). The *Z*/*E* isomer ratio averaged 4:1 as determined by ^{1}H NMR, and no attempt was made to separate the mixture.

Equilibration of Cycloundecene-1-carboxylic Acid 1 and 2 (*n* = 9). A solution of 200 mg of acid per 3.0 mL of triethylamine and 3.0 mL of acetic anhydride was allowed to equilibrate at 50.2, 61.0, 70.1, and 82.1 °C (±0.5 °C) for 10 days. Water baths were equilibrated and covered with a thin layer of unused vacuum pump oil to avoid water loss due to evaporation. After the allotted time, a 1-mL excess of ice-cold concentrated HCl (e.g., if 3 mL of triethylamine was used for isomerization, 4 mL of HCl was required) was added dropwise to the reaction mixture which was suspended in an ice bath. White clouds of triethylamine hydrochloride immediately formed, the mixture was carefully shaken and the reaction vessel cooled for 10 min at ice bath temperature. The mixture was diluted with 30 mL of H_2O and transferred to a 125-mL separatory funnel, and the reaction vessel was rinsed with ether and these rinses were added to the separatory funnel. The mixture was further extracted with two 30-mL aliquots of ether which was extracted twice with 30 mL of 5% NaOH. The aqueous phase was acidified with ice-cold HCl to pH 3, the acids were extracted twice with 20 mL of ice-cold ether, the combined ether extracts were dried over Na_2SO_4, and concentration of the ether solution with a rotary evaporator gave the solid acids. The average recovery of acids for this procedure was approximately 95%. The mixture of acids was methylated by adding an ether solution of diazomethane until evolution of nitrogen gas ceased, and the solution was reduced to 0.2 mL. Pure preparation of both isomers was used to identify retention times by coinjection. Typical gas chromatography retention times were 5.65 min for the *E* methyl ester isomer and 4.80 min for the *Z* methyl ester isomer. Equilibrium ratios were determined from the areas of each peak, and equilibrium constants are given in Table II. Typical GC conditions follow: inlet temperature 300 °C; column (12 ft × ⅛ in. i.d.; 5% SE-30 on Chromosorb W); temperature program 160–205 °C at 5 °C/min; detector temperature 200 °C; filament current 225 μA; He flow rate 4.0 mL/min; manifold temperature 280 °C; sample size 0.2 μL; and attenuation 16.

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Registry No.—1(n = 9), 63657-92-1; 1(n = 10), 63657-93-2; 2(n = 7), 63657-94-3; 2(n = 8), 63657-95-4; 2(n = 9), 63657-96-5; 2(n = 10), 63657-97-6; 4(n = 7), 4017-57-6; 4(n = 8), 4017-58-7; 4(n = 9), 4017-59-8; 4(n = 10), 4017-60-1; hydrazine, 302-01-2; Cl_2, 7782-50-5.

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Pyrolysis of Esters. 27. Pyrolysis of Lactones[1,2]

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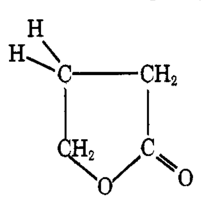
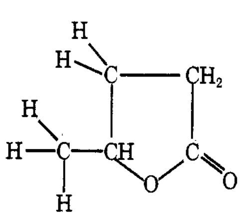
In order to demonstrate the concerted nature of the elimination reaction in the pyrolysis of esters, a series of lactones containing 5, 7, 10, and 12 atoms in the ring were pyrolyzed. At 520 °C γ-butyrolactone and γ-methyl-γ-butyrolactone were essentially stable and only a negligible amount of decomposition occurred at 590 °C. The ε-caprolactone pyrolyzed to the extent of 5% at 520 °C and 53% at 590 °C. In contrast, ε-methyl-ε-caprolactone at 520 °C gave an 89% yield of heptenoic acid. The lactone from 9-hydroxynonanoic acid gave a 92% yield of 8-nonenoic acid at 520 °C, while the lactone from 11-hydroxyhendecanoic acid gave an 86% yield of 10-hendecenoic acid at 520 °C. Although the γ-butyrolactone has a hydrogen atom located in the β position relative to the ether oxygen, the models show that the formation of the hydrogen–oxygen bridge to complete the necessary quasi-six-membered ring is not probable. With the ε-caprolactone, examination of the models shows that the hydrogen atom and the carbonyl oxygen can be made to come within bonding distance with some ring strain. In the larger ring lactones, the quasi-six-membered ring can be formed with little or no strain. These results not only support the quasi-six-membered ring mechanism for ester pyrolysis, but also represent a convenient synthesis of several unsaturated acids.

In 1938 Hurd and Blunck proposed that esters pyrolyze by a unimolecular cyclic mechanism.[4] Although the exact details of the mechanism of this reaction have still not been determined, a considerable amount of circumstantial evidence has been built up to substantiate the cyclic nature of the reaction. Evidence for the four-center-type mechanism includes first-order kinetics,[5] negative entropy of activation, and a preferred cis elimination.[6,7] Pyrolysis of methyl *cis*-2-acetoxycyclohexanecarboxylate at 435 °C gave only methyl 2-cyclohexenecarboxylate and no methyl 1-cyclohexenecarboxylate.[7] On the other hand, the pyrolysate from methyl *trans*-2-acetoxycyclohexanecarboxylate contained 97% of the conjugated ester and only 3% of the unconjugated isomer.[7] Under these controlled conditions, there was no trans elimination. However, at higher temperatures it appears that a trans elimination can take place. For example, Alexander and Mudrak[6] showed that both the *cis*- and *trans*-2-methylindanyl acetate gave the same product, 2-methylindene; however, a temperature approximately 200 °C higher was required for the decomposition of the trans isomer.

One of the problems that remains in ester pyrolysis is to demonstrate in a more definitive manner that the reaction is concerted, i.e., that the new hydrogen–oxygen bond is partly formed before the complete cleavage of the original carbon–oxygen bond. One can write several mechanisms that would fit the kinetics and the stereochemistry that would not involve the simultaneous bond-making and bond-breaking processes. It appeared, therefore, that it would be interesting to study a series of compounds in which the new oxygen–hydrogen bond could not form prior to cleavage of the original carbon–oxygen bond. The small-ring lactones appear to meet this criterion. For example, γ-butyrolactone (**1a**), which is a cyclic ester, does contain a β-hydrogen in the alkyl portion, but because of the constraint of the five-membered ring there is no possible close approach of the hydrogen atom to the oxygen, until the ring is cleaved. In other words, the hydrogen and the carbonyl are pointing away from the ring, and, therefore, there is considerable distance between the hydrogen and oxygen. We reasoned, therefore, that the pyrolysis of the lactones would clearly establish whether prior or simultaneous bond making between the carbonyl and the hydrogen is necessary for the cleavage of the ester.



1a



1b

A number of workers have studied the pyrolysis of lactones, but none of the examples in the literature are completely related to the present work. For instance, in 1889 Fittig et al.[8,9]