

**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;  $\text{Cl}_2$ , 7782-50-5.

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## Pyrolysis of Esters. 27. Pyrolysis of Lactones<sup>1,2</sup>

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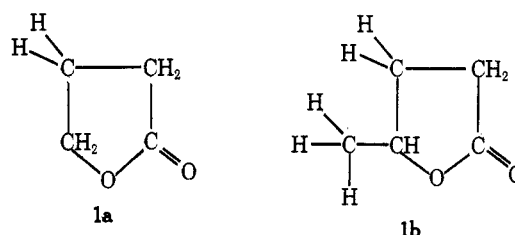
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In order to demonstrate the concerted nature of the elimination reaction in the pyrolysis of esters, a series of lactones containing 5, 7, 10, and 12 atoms in the ring were pyrolyzed. At 520 °C  $\gamma$ -butyrolactone and  $\gamma$ -methyl- $\gamma$ -butyrolactone were essentially stable and only a negligible amount of decomposition occurred at 590 °C. The  $\epsilon$ -caprolactone pyrolyzed to the extent of 5% at 520 °C and 53% at 590 °C. In contrast,  $\epsilon$ -methyl- $\epsilon$ -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  $\gamma$ -butyrolactone has a hydrogen atom located in the  $\beta$  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  $\epsilon$ -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.<sup>4</sup> 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,<sup>5</sup> negative entropy of activation, and a preferred *cis* elimination.<sup>6,7</sup> Pyrolysis of methyl *cis*-2-acetoxycyclohexanecarboxylate at 435 °C gave only methyl 2-cyclohexenecarboxylate and no methyl 1-cyclohexenecarboxylate.<sup>7</sup> On the other hand, the pyrolysate from methyl *trans*-2-acetoxycyclohexanecarboxylate contained 97% of the conjugated ester and only 3% of the unconjugated isomer.<sup>7</sup> 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<sup>6</sup> 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,  $\gamma$ -butyrolactone (**1a**), which is a cyclic



ester, does contain a  $\beta$ -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.

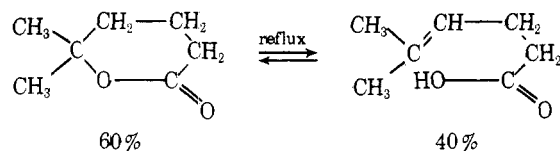
A number of workers have studied the pyrolysis of lactones, but none of the examples in the literature are completely related to the present work. For instance, in 1889 Fittig et al.<sup>8,9</sup>

Table I

Lactone	No. of atoms in ring	Product	Extent of pyrolysis, %	
			at 520 °C	at 590 °C
$\gamma$ -Butyrolactone (1a)	5		0	Trace
$\gamma$ -Methyl- $\gamma$ -butyrolactone (1b)	5		Trace	Trace
$\epsilon$ -Caprolactone (2)	7	5-Hexenoic acid	5	53
$\epsilon$ -Methyl- $\epsilon$ -caprolactone (4)	7	6-Heptenoic acid	89	
9-Hydroxynonanoic acid lactone (3)	10	8-Nonenoic acid	92	
11-Hydroxyhendecanoic acid lactone (5)	12	10-Hendecenoic acid	86	

reported that the  $\gamma$ -ethyl- $\gamma$ -butyrolactone- $\beta$ -carboxylic acid decomposed at 200–300 °C to yield 3-hexenoic acid. Linstead et al.<sup>10</sup> improved the method to the point where it was a practical synthetic procedure. The pyrolysis of a  $\beta$ -lactone usually gives carbon dioxide and the corresponding unsaturated compound.<sup>11–13</sup>

The pyrolysis of an  $\alpha$ -keto- $\gamma$ -lactone can occur either with the loss of carbon monoxide and carbon dioxide to give an olefin or with loss of carbon dioxide to form an aldehyde.<sup>14–16</sup> Linstead<sup>17</sup> reported that when  $\gamma$ -caprolactone or  $\gamma,\gamma$ -dimethyl- $\gamma$ -butyrolactone was heated under reflux alone or with 60% sulfuric acid for periods up to 50 h, 1% or less of titratable acidic material was formed. However, Schutte and Thomas,<sup>18</sup> in determining the vapor pressure of  $\gamma$ -valerolactone, observed a small amount of carbon dioxide formed, but no ethylenic hydrocarbons. Finally, Linstead and Rydon<sup>19</sup> reported that when either pure 5-methyl-4-hexenoic acid or  $\delta,\delta$ -dimethyl- $\delta$ -valerolactone was heated under reflux an equilibrium mixture containing 40% of the acid and 60% of the lactone

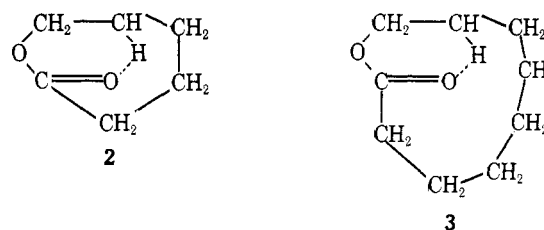


resulted. They concluded: "There is no doubt that the lactone and the acid become interconvertible above 200°".

Since all the previous lactone pyrolysis studies were done by prolonged heating in the liquid phase, we felt that it was worthwhile to study the pyrolysis of a series of lactones in the vapor state to determine their stabilities and reactions. When  $\gamma$ -butyrolactone (1a) was pyrolyzed at 590 °C, a nearly colorless pyrolysate was obtained in essentially quantitative yield. The recovered lactone had the same refractive index as the starting material and an identical infrared spectrum. There was no evidence that an olefinic material was produced, and a titration indicated that a negligible amount of titratable acid was produced. We concluded, therefore, that essentially no pyrolysis took place under these conditions.

Under very similar conditions,  $\gamma$ -valerolactone (1b) was pyrolyzed at 590 °C to form a pale-yellow liquid pyrolysate, accompanied by some carbonization in the pyrolysis tube. A total 1.7% yield of carbon dioxide was collected in an Ascarite tube and 8.6% of the material was lost as a noncondensable gas. However, the refractive index of the pyrolysate was essentially the same as the starting material, but contained only 3.7% of a titratable acid. This acidic material was tentatively identified as pentenoic acid. This result would indicate that there was a small amount of pyrolysis at this temperature, but the actual mechanism of this reaction is unclear and certainly may have been acid catalyzed. When the pyrolysis of the  $\gamma$ -valerolactone was carried out at 540 °C, the pyrolysate was water-white and had essentially the identical properties of the starting material. Essentially no carbon dioxide or olefin was formed, and a negligible amount of titratable acid was detected. Thus, under the conditions that most esters would pyrolyze, even the  $\gamma$ -valerolactone is quite stable.

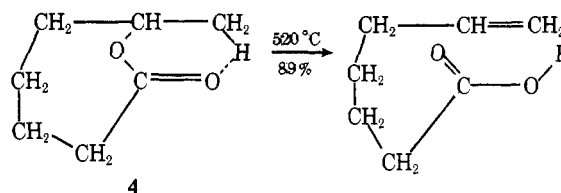
A study of the Fisher–Taylor–Hirschfelder models led to the conclusion that if the ring of the lactone was large enough the carbonyl could, indeed, get close enough to the  $\beta$ -hydrogen atom to form the quasi-six-membered ring necessary for the operation of an ester pyrolysis. A study of these models further indicated that in a seven-membered lactone, such as 2, it would be extremely difficult to form the cyclic six-membered intermediate. However, in a nine-membered lactone, such as 3, the ring could form with sufficient ease to predict that this



lactone would pyrolyze fairly normally. Obviously, then, any lactone that contains more than nine members in the ring would also pyrolyze quite readily.

For these reasons, we have studied the pyrolysis of  $\xi$ -caprolactone<sup>20</sup> (2). When 2 was pyrolyzed at 590 °C, 25% of the material was lost as a gas, and the liquid pyrolysate contained 53% of a titratable acid, calculated as hexenoic acid. At 560 °C 14% of the material was lost, and the pyrolysate contained only 30% acid. At 520 °C essentially no material was lost, but the pyrolysate contained only 5% titratable acid. The acid produced was identified as hexenoic acid, first by an infrared analysis which gave strong absorption bands at 1410, 987–990, and 910–913  $\text{cm}^{-1}$ . There was no evidence in the infrared spectrum of a methyl group, or a cis or trans double bond, all of which indicated that little or no isomerism of the 5-hexenoic acid to the 4-hexenoic acid had occurred. The 5-hexenoic acid was isolated and converted to the known *p*-toluide and the *p*-bromophenacyl ester.

The Fisher–Hirschfelder models indicated that, in the case of  $\xi$ -methyl- $\xi$ -caprolactone (4), the hydrogen atom on the methyl group was close enough to the carbonyl of the ester to permit the formation of the transient six-membered ring. Thus, when 4 was pyrolyzed at 520 °C, the pyrolysate con-



tained 89% of titratable acid, calculated as heptenoic acid. The infrared analysis of the mixture showed the presence of the terminal vinyl group and an estimation that the mixture contained 7% of a compound which contained a methyl group, presumably the original lactone; the presence of the terminal vinyl group was very evident. The 6-heptenoic acid was further identified by conversion to the known *p*-toluide derivative.

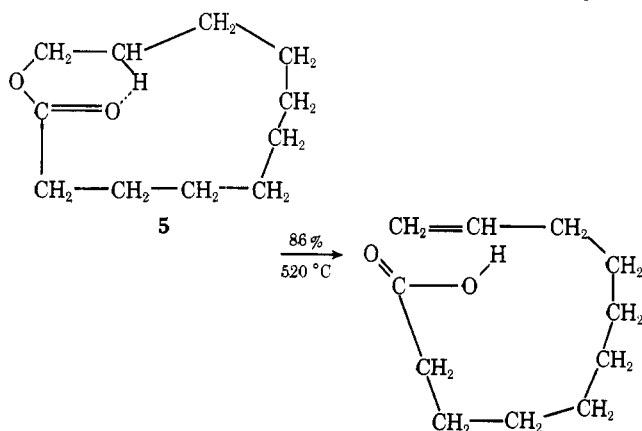
The Fisher–Hirschfelder models indicated that, as the size of the lactone increased, there was a decreasing difficulty in getting the  $\beta$ -hydrogen and the carbonyl close together. In

order to demonstrate that the large lactones would, indeed, pyrolyze in a manner similar to an open-chain ester, we decided to study the pyrolysis of the lactones containing 10 and 12 atoms in the ring. Although Spanagel and Carothers<sup>21</sup> have prepared a large number of lactones by the thermal depolymerization of polyesters, and Stoll and Rouve<sup>22</sup> have prepared a series of lactones by the high-dilution cyclization of  $\Omega$ -hydroxy acids in boiling benzene under the influence of acid catalysts, both of these methods produced large quantities of dimers and trimers, which made the monomeric lactones difficult to purify. The method that appeared to be most suitable was the cyclization of the  $\Omega$ -bromo acids by the method of Hunsdiecker et al.<sup>23</sup>

By their method, methyl hydrogen sebacate was prepared in a 31% yield by the partial hydrolysis of dimethyl sebacate. The silver salt of this acid, which contained a small amount of the disilver sebacate, was converted into the methyl 9-bromonanoate by heating the silver salt in carbon tetrachloride with an excess of bromine. The resulting ester was converted into the corresponding nonanoic acid in a 75% yield by treatment with hydrogen bromide in glacial acetic acid. In an apparatus that was somewhat simpler than that described by Hunsdiecker and Erlbach,<sup>23</sup> the 9-hydroxynonanoic acid lactone (3) was prepared in a 32% yield by the high-dilution technique. Although a 59% yield of residue was obtained from the reaction, there was an indication that a considerable amount of dimers, trimers, and higher esters were formed. In a very similar procedure, the lactone 5 from 11-hydroxyhendecanoic acid was produced. By a modification of the procedure of Ashton and Smith,<sup>24</sup> 11-bromohendecanoic acid was prepared by the addition of hydrogen bromide to 10-hendecenoic acid in a 35% yield. Cyclization by the procedure indicated previously produced the 12-membered lactone 5 in an 86% yield.

Pyrolysis of these two large-ring lactones demonstrated that they would pyrolyze very normally. Thus, when the ten-membered lactone 3 from 9-hydroxynonanoic acid was pyrolyzed at 520 °C, 93% of titratable acid was obtained and only 7% of the lactone was recovered. The product which was obtained in a 68% yield was identified as 8-nonenoic acid by its infrared spectrum, which was very similar to that of the 5-hexenoic acid previously discussed, and by conversion to the known *p*-toluide derivative. There was no evidence that any 7-nonenoic acid was produced.

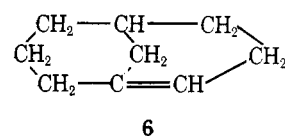
In a similar manner, the pyrolysis of the 12-membered lactone 5 from 11-hydroxyhendecanoic acid at 520 °C gave a



pyrolysate containing 86% titratable acid, which yielded 58% of the pure 10-hendecenoic acid. The identity of this acid was established by the infrared analysis and by conversion to the known 10,11-dibromohendecanoic acid.

We have thus demonstrated that the small-ring lactones will not pyrolyze as normal esters because the  $\beta$ -hydrogen atom and the carbonyl can not conveniently get together in

the cyclic transition state required for ester pyrolysis. The larger-ring lactones, however, pyrolyze very similarly to the open-chain esters, since this cyclic transition state can take place. The medium-size lactones make an interesting transition between these two extremes in that the compounds begin to pyrolyze just as one would predict from the Fisher-Hirschfelder models. In a sense, the lactones would be governed by Bredt's rule, since there is a double bond at the bridgehead when one begins to form the cyclic transition state. A modern statement of Bredt's rule in qualitative terms<sup>25</sup> is as follows: "A double bond cannot be placed with one terminal at the bridgehead of a bridge ring system, unless the rings are large enough to accommodate the double bond without excessive strain". As an indication of the strain that can be accommodated in such a bridge system, bicyclo[3.3.1]non-1-ene (6) has been synthesized.<sup>26</sup> This bicyclo olefin represents two



fused six-membered rings with only a single atom connecting the two bridge heads. The intermediate for the pyrolysis of  $\xi$ -caprolactone (2) would involve fused six- and seven-membered rings with the hydrogen atom and carbonyl oxygen connecting the two "bridge head" atoms in 2a. This arrangement apparently is not impossible, but does involve a considerable increase in strain over that involved in a normal ester pyrolysis.

On the other hand,  $\xi$ -methyl- $\xi$ -caprolactone (4) involves the fused six- and seven-membered rings where the ether oxygen represents the single atom between the two bridgehead carbons in 4a. This system involves less strain, and, therefore, pyrolysis occurs fairly readily at 520 °C. It is interesting that this is a pyrolysis in which the direction of elimination is made to go exclusively to the methyl group, since the ring which would result in the formation of the internal double bond has considerably more strain. We conclude, therefore, that this study is an excellent demonstration of the involvement of the six-membered ring transition state in the pyrolysis of esters. The shift from stability of the lactones to normal ester pyrolysis takes place in the order and degree that one would predict from a study of the Fisher-Hirschfelder models.

### Experimental Section<sup>27</sup>

**Pyrolysis of  $\gamma$ -Butyrolactone (1a).** A pyrolysis tube packed with Vycor Raschig rings was used in the standard pyrolysis apparatus.<sup>28</sup> After nitrogen had been bubbled through the material to be pyrolyzed for several minutes, 20.7 g (0.24 mol) of commercially available  $\gamma$ -butyrolactone (1a) (Matheson), bp 83.5 °C (12 mm),  $n_D^{25}$  1.4340 [reported<sup>29</sup> bp 83.5 °C (12 mm),  $n_D^{25}$  1.4354], was dropped at the rate of 0.54 g/min through the pyrolysis tube at 590 °C to yield 19.3 g of an almost colorless pyrolysate,  $n_D^{25}$  1.4340. Only a trace amount of carbon was deposited in the pyrolysis tube. Titration at -5 °C with standard sodium hydroxide solution of a small portion of the pyrolysate dissolved in 50% ethanol indicated the presence of a maximum of 0.28% titratable acid.

**Pyrolysis of  $\gamma$ -Valerolactone (1b).** Two "cold finger" condensers and a tube packed with Ascarite were attached in that order to the exhaust vent of the standard pyrolysis apparatus. After nitrogen had been bubbled through the material to be pyrolyzed for several minutes, 63.7 g (0.636 mol) of distilled  $\gamma$ -valerolactone (1b), (Eastman Kodak practical grade), bp 103–103.5 °C (29 mm),  $n_D^{25}$  1.4310–1.4312 [reported<sup>29</sup> bp 102–103 °C (28 mm),  $n_D^{20}$  1.4322], was dropped at the rate of 0.50 g/min through the pyrolysis tube at 590 °C to yield 58.2 g (91% recovery) of pale-yellow liquid pyrolysate,  $n_D^{25}$  1.4308. A black deposit of carbon was found on the pyrolysis tube packing. The Ascarite tube absorbed 1.1 g (1.7%) of carbon dioxide, and about 1 mL of a colorless liquid was found in the first cold finger.

The liquid in the cold finger evaporated quite rapidly when kept in an ice bath at 1–2 °C and quite slowly when kept in a salt-ice bath at -5 to -10 °C. A small amount of this liquid decolorized a solution

of bromine in carbon tetrachloride without the evolution of hydrogen bromide. Titration of a small portion of the pyrolysate as described previously indicated the presence of 3.7% of titratable acid.

**Pyrolysis of  $\epsilon$ -Caprolactone (2).** A sample of 6-hydroxyhexanoic acid lactone (2)<sup>20</sup> was fractionated through a 17-in., helix-packed column to obtain a purified sample, bp 50–51.5 °C (0.1 mm),  $n_{D}^{25}$  1.4612–1.4615 [reported<sup>30</sup> bp 98–99 °C (2 mm),  $n_{D}^{24}$  1.4608]. After nitrogen had been bubbled through the material to be pyrolyzed for several minutes, the standard pyrolysis apparatus was used to drop 25.1 g (0.22 mol) of 2 at the rate of 0.81 g/min through the pyrolysis tube at 580 °C to yield 18.7 g (25.5% loss) of a pale-yellow liquid pyrolysate,  $n_{D}^{25}$  1.4470. A black deposit of carbon was found on the pyrolysis tube packing. An Ascarite-filled tube attached to the exhaust vent of the pyrolysis apparatus absorbed 0.91 g (3.6%) of carbon dioxide. A titration indicated that the pyrolysate contained 52.8% titratable acid (calculated as hexenoic acid).

In an attempt to isolate a pure sample of the 5-hexenoic acid for characterization, the pyrolysate was fractionated through a 17-in., helix-packed column. Since the lactone and acid boil within 10–13 °C of one another at 10 mm, the pyrolysate was fractionated at as high a pressure as was practicable in order to secure a maximum difference in boiling points. Only a poor separation could be effected to yield 3.48 g of impure hexenoic acid, bp 95–99.3 °C (9–9.5 mm),  $n_{D}^{25}$  1.4390–1.4394 [reported<sup>31</sup> bp 107 °C (17 mm),  $n_{D}^{20}$  1.4343]. Titration in cold ethanol, followed by saponification with an excess of base and back titration showed that this impure sample contained 17% lactone.

In a similar pyrolysis at 560 °C, 14.7 g (0.129 mol) of  $\epsilon$ -caprolactone (2) yielded 12.5 g (14.6% loss) of a yellow liquid pyrolysate,  $n_{D}^{25}$  1.4526. Less charring occurred and a titration indicated that the pyrolysate contained 30.3% titratable acid. In a similar pyrolysis at 520 °C the pyrolysate contained only 5% titratable acid.

Infrared spectra of solutions of 6% of the distilled hexenoic acid in carbon tetrachloride or of 10% of the acid in carbon disulfide showed strong absorption bands at 1410, 987–990, and 910–113  $\text{cm}^{-1}$  as good evidence for the presence of a vinyl group. No band was noted at 1370–1385  $\text{cm}^{-1}$ , indicative of a methyl group, nor a band at 960–970  $\text{cm}^{-1}$ , indicative of a trans double bond, nor at 690  $\text{cm}^{-1}$ , indicative of a cis double bond.

Attempts to prepare the *p*-toluide of the 5-hexenoic acid by the procedure of Shriner and Fuson<sup>32</sup> or Fichter and Pfister<sup>33</sup> resulted in a dark brown oil. Finally, a mixture of 0.53 g (0.005 mol) of the impure acid and 1.2 g (0.01 mol) of purified thionyl chloride was heated under gentle reflux for 35 min. After the excess thionyl chloride had been removed by distillation under reduced pressure, a solution of 1.1 g (0.01 mol) of *p*-toluidine in dry benzene was added and the mixture was heated for 10 min. After the mixture was cooled, the *p*-toluidine hydrochloride was removed by filtration and washed with benzene. The combined filtrates were extracted successively with water, 5% hydrochloric acid, and a 5% sodium hydroxide solution. Removal of the benzene by evaporation on a steam bath yielded 0.41 g (41%) of a dark brown low-melting solid. Repeated extraction of the residue with petroleum ether produced a light-yellow solution. Evaporation of the solvent, plus cooling, produced a solid material. Recrystallization of this solid from petroleum ether gave a white *p*-toluide, mp 57.6–58.2 °C (reported<sup>31</sup> mp 58 °C).

By the directions of Shriner and Fuson,<sup>34</sup> 0.57 g (0.005 mol) of the impure 5-hexenoic acid was mixed with 2 mL of water and neutralized with a 5% sodium hydroxide solution. After 1.39 g (0.005 mol) of *p*-bromophenacyl bromide and 10 mL of ethanol were added, the mixture was heated under reflux for 75 min. The precipitate which separated from the cooled mixture was removed by filtration, and recrystallized from ethanol to produce white plates, mp 49–49.2 °C.

Anal. Calcd for  $\text{C}_{14}\text{H}_{15}\text{BrO}_3$ : C, 54.03; H, 4.86. Found: C, 54.29; H, 4.92.

**Pyrolysis of  $\epsilon$ -Methyl- $\epsilon$ -caprolactone (4).** A sample of 6-hydroxyheptanoic acid lactone (4)<sup>20</sup> was fractionated through a 17-in., helix-packed column to produce a purified sample, bp 52 °C (0.41 mm),  $n_{D}^{25}$  1.4564. After nitrogen had been bubbled through the material to be pyrolyzed for several minutes, the standard pyrolysis apparatus was used to drop 14.9 g (0.116 mol) of  $\epsilon$ -methyl- $\epsilon$ -caprolactone (4) at the rate of 0.76 g/min through the pyrolysis tube at 520 °C to yield 14.0 g of a pale-yellow, liquid pyrolysate. (A very small amount of carbon was found deposited in the pyrolysis tube.) A titration indicated that the pyrolysate contained 89.1% titratable acid (calculated as heptenoic acid).

To isolate a sample of pure 6-heptenoic acid, the pyrolysate was extracted by a procedure similar to that described for the 5-hexenoic acid. The residue which was obtained at the end of the operation was dried in a vacuum desiccator over phosphorus pentoxide to yield 7.65 g of impure 6-heptenoic acid,  $n_{D}^{14.9}$  1.4430 (reported<sup>35</sup>  $n_{D}^{14.9}$  1.4404).

(Titration indicated that this sample of acid contained 7% of the lactone.)

The infrared spectra of solutions of the acid in carbon tetrachloride and carbon disulfide showed strong absorption bands at 1410, 987–990, and 910–913  $\text{cm}^{-1}$  (good evidence for the presence of the vinyl group in the compound) and no bands were found in the regions which would indicate the presence of a methyl group or of a cis or trans double bond in the molecule. From these data it may be concluded that pyrolysis of the lactone resulted in the formation of all or mostly 6-heptenoic acid and that little or no isomeric 5-heptenoic acid was produced, either by pyrolysis or isomerization.

By a procedure similar to that described for 5-hexenoic acid, 1.28 g (0.01 mol) of the impure 6-heptenoic acid yielded 2.10 g (97%) of the crude brown product which was treated with charcoal and recrystallized from ethanol to yield pure 6-heptenoic acid *p*-toluide, mp 59–59.3 °C (reported<sup>35</sup> mp 59.6 °C).

**Pyrolysis of 9-Hydroxynonanoic Acid Lactone (3).** The desired lactone from 9-hydroxynonanoic acid was prepared essentially by the method of Hunsdiecker and Hunsdiecker.<sup>23</sup> Methyl 9-bromononanoate, bp 87–91 °C (0.2–0.3 mm) [reported<sup>23</sup> bp 131 °C (2 mm)], was prepared in a 49% yield from the silver salt of methyl hydrogen sebacate. Treatment of this ester with hydrogen bromide in glacial acetic acid gave a 75% yield of the 9-bromononanoic acid, mp 32.4–32.8 °C (reported<sup>23</sup> mp 34 °C). With an amount of material that was two and a half times larger than that described by Hunsdiecker and Erlbach,<sup>23</sup> 23.75 g (0.1 mol) of the bromo acid was added to 7.5 L of methyl ethyl ketone containing 250 g of oven-dried potassium carbonate by means of a woolen thread to a high-dilution apparatus over a 56-h period. The reaction mixture was filtered and the solvent was removed from the filtrate by distillation. The residue was extracted with benzene, and removal of the benzene by evaporation gave a yellow liquid residue, which was recrystallized three times from *n*-pentane and once from methanol to yield 9.2 g (59%) of impure 3, mp 24.2–31.7 °C (reported<sup>23</sup> 56% yield, mp 23–30 °C). Fractionation of this material through a 5-in., helix-packed column gave a sample of pure 9-hydroxynonanoic acid lactone (3), bp 75 °C (5 mm), mp 30.7–31.2 °C [reported<sup>28</sup> bp 93 °C (13 mm), mp 31–31.5 °C].

While the delivery vessel was immersed in hot water, 6.45 g (0.0413 mol) of the lactone 3 was dropped at the rate of 0.68 g/min through the pyrolysis tube at 520 °C to yield 5.75 g of a pale-yellow, liquid pyrolysate. A very small amount of carbon was deposited at the point of vaporization in the pyrolysis tube. Titration at 5 °C of a small portion of the pyrolysate dissolved in 80% ethanol, followed by saponification with an excess of base and back titration, indicated that the pyrolysate contained 93% titratable acid (calculated as nonenoic acid) and 7% saponifiable lactone.

The acid was separated from the lactone by extraction, as was described previously, by the use of a 0.5 N sodium bicarbonate solution and then 1 N hydrochloric acid. After the final ether extracts had been dried over sodium sulfate, the solvent was removed by distillation under reduced pressure and the residue was dried in a vacuum desiccator over phosphorus pentoxide to yield 3.88 g (68% yield based on weight of pyrolysate) of 8-nonenoic acid,  $n_{D}^{15}$  1.4488 (reported<sup>35</sup>  $n_{D}^{15}$  1.4492). One drop of this acid readily decolorized a solution of bromine in carbon tetrachloride with no evolution of hydrogen bromide.

The infrared spectra of solutions of the acid in carbon tetrachloride and in carbon disulfide were almost identical to those described for heptenoic acid. Hence, it was concluded that the product contained a terminal double bond and that little or no 7-nonenoic acid was produced by pyrolysis or by isomerization.

The *p*-toluide derivative was prepared by the method described previously from 0.78 g (0.005 mol) of the 8-nonenoic acid. The petroleum ether extract yielded 1.08 g (88%) of slightly impure material which was treated with decolorizing charcoal and recrystallized twice from petroleum ether (67 °C) to yield 8-nonenoic-*p*-toluide, mp 67.3–67.6 °C (reported<sup>35</sup> mp 68 °C).

**Pyrolysis of 11-Hydroxyhendecanoic Acid Lactone (5).** The directions given by Ashton and Smith<sup>24</sup> were followed both for the purification of the petroleum ether and 10-hendecenoic acid, as well as the formation of the 11-bromohendecanoic acid. Thus, the addition of hydrogen bromide to 10-hendecenoic acid in petroleum ether gave a 35% yield of 11-bromohendecanoic acid, mp 51.8–52.4 °C (reported<sup>24</sup> mp 49.5–51 °C). By a procedure similar to that for 9-hydroxynonanoic acid lactone, as described above, the 11-bromohendecanoic acid was converted in an 86% yield to the corresponding lactone 5, bp 69–72 °C (0.92 mm),  $n_{D}^{25}$  1.4683 [reported<sup>24</sup> bp 103 °C (5 mm),  $n_{D}^{20}$  1.4716].

The standard pyrolysis apparatus modified as described above was used to drop 7.59 g (0.0412 mol) of 11-hydroxyhendecanoic acid lactone (5) at the rate of 0.95 g/min through the pyrolysis tube at 520 °C

to yield 6.87 g of pale-yellow, liquid pyrolysate. A very small amount of carbon was deposited in the pyrolysis tube. Titration at 0 °C of a small portion of the pyrolysate dissolved in 95% ethanol indicated that the pyrolysate contained 86% titratable acid (calculated as hendecenoic acid).

The acid was separated from the lactone by extraction, as described previously, by the use of a 0.5 N sodium bicarbonate solution and then 0.5 N hydrochloric acid. The solvent was removed from the final ether extracts by distillation under reduced pressure and the residue was dried in a vacuum desiccator to yield 3.98 g (58% based on the weight of the pyrolysate) of 10-hendecenoic acid, mp 17–19.6 °C,  $n_D^{25}$  1.4465 [reported<sup>36</sup> mp 25.5 °C,  $n_D^{24}$  1.44642]. A mixture melting point determination with an authentic sample of 10-hendecenoic acid,  $n_D^{25}$  1.4463, exhibited a melting point of 18.5–21.3 °C.

While a solution of 2.28 g (0.011 mol) of 10-hendecenoic acid in 10 mL of purified petroleum ether was stirred in an ice bath, 2.2 g (0.027 mol) of bromine was added dropwise. A crystalline precipitate was collected by filtration and recrystallized from petroleum ether to yield 2.24 g (56%) of 10,11-dibromohendecanoic acid, mp 38.3–39.6 °C (reported<sup>36</sup> mp 38.5 °C). A mixture melting point determination with an authentic sample of the dibromo compound showed no depression.

**Registry No.**—1a, 96-48-0; 1b, 108-29-2; 2, 502-44-3; 4, 2549-59-9; 3, 6008-27-1; 5, 1725-03-7; 5-hexenoic acid, 1577-22-6; *p*-bromophenacyl bromide, 99-73-0; *p*-bromophenacyl 5-hexenoate, 63657-88-5; 6-heptenoic acid, 1119-60-4.

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## Pyrolysis of Unsaturated Compounds. 1. Pyrolysis of Vinyl Ethers<sup>1,2</sup>

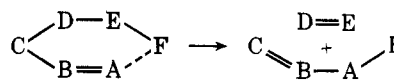
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Pyrolyses of vinyl ethers proceed at a temperature 40–50 °C lower than the corresponding esters. Thus, the pyrolysis of *n*-butyl vinyl ether at 480 °C gave 1-butene (71%), acetaldehyde (42%), and recovered vinyl ether (8%), while at 450 °C a 45% recovery of starting material was noted. Similarly, 2-ethylhexyl vinyl ether at 450 °C gave a 47% recovery of starting vinyl ether plus a 20% yield of 2-ethyl-1-hexene and a 29% yield of acetaldehyde. Pyrolysis of 2-ethoxy-1-butene at 460 °C gave nearly a quantitative conversion to methyl ethyl ketone and ethylene, while at 425 °C gave a 73% conversion to ketone and a 17% recovery of starting vinyl ether. Pyrolysis of  $\beta$ -butoxyethyl acetate at 520 °C gave a 65% yield of 1-butene and a 46% yield of acetaldehyde, but only a 12% yield of *n*-butyl vinyl ether and a 14% recovery of starting ester. Apparently, the ester pyrolyzes to give the intermediate vinyl ether, but at the high temperature (74 °C above the temperature required for 50% pyrolysis of the vinyl ether) the *n*-butyl vinyl ether undergoes extensive secondary pyrolysis. On the other hand, the corresponding  $\alpha$ -butoxyethyl acetate pyrolyzes at 380 °C to give a 43% yield of *n*-butyl vinyl ether with <4% secondary pyrolysis to 1-butene and acetaldehyde. Under temperatures at which other vinyl ethers pyrolyze methyl vinyl ether is relatively stable, but at 500 °C a 15% yield of propionaldehyde was noted. These results support the concept that unsaturated materials decompose by a concerted molecular mechanism in which the cyclic six-membered transition state resembles the products more than the starting materials.

Previous work in these laboratories has shown that pyrolysis of esters was a very excellent synthetic tool for the preparation of highly strained dienes,<sup>3,4</sup> isomers of aromatic compounds,<sup>5–7</sup> and highly reactive monomers.<sup>8–10</sup> Since we were able to confirm that the mechanism involved a quasi six-membered ring intermediate,<sup>11–13</sup> we became interested in finding out what other atoms would allow the six-membered cyclic mechanism to operate. In ester pyrolysis, A and C are



oxygen atoms, but pyrolysis of compounds with other atoms in these two positions are well known. For instance, the Chugaev reaction which involves the pyrolysis of a xanthate ester involves a sulfur atom at position A. Nace and O'Connor<sup>14</sup> proposed that the fact the xanthates pyrolyzed at a lower