Pyrolysis of Unsaturated Compounds. 2. Pyrolysis of Ketones[1,2]

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In order to compare the ease of pyrolysis of ketones with that of esters, a series of ketones was pyrolyzed in an apparatus commonly used for preparative ester pyrolysis. Thus, when heptane-2,6-dione was pyrolyzed at 650 °C, the major products of pyrolysis were methyl vinyl ketone (17%) and acetone (22%). Since 66% of the starting diketone was recovered unchanged, the yields of acetone and methyl vinyl ketone based on unrecovered material were 61 and 45%, respectively. In a similar experiment at 650 °C, pyrolysis of methyl neopentyl ketone gave a 17% yield of acetone and an 18% yield of isobutylene. Since 61% of the methyl neopentyl ketone was recovered unchanged, the yields of acetone and isobutylene, based on unrecovered material, were 44 and 46%, respectively. When methyl isobutyl ketone was pyrolyzed at 650 °C, 75% of the ketone was recovered unchanged and the major products were propylene (10%) and acetone (7%); however, at the same time an 8% yield of isobutylene was obtained. Pyrolysis of methyl n-propyl ketone at 650 °C gave an 87% recovery of the ketone plus a 6% yield of acetone and a 3% yield of ethylene, as well as a 5% yield of methyl vinyl ketone plus some propylene. Thus, it appears that a ketone is considerably more thermally stable than an ester, requiring some 150 °C higher temperature for a comparable extent of decomposition.

Since previous work in these laboratories had shown that pyrolysis of esters was a very excellent synthetic tool for the preparation of a wide variety of strained dienes,[4] isomers of aromatic compounds,[5] and highly reactive monomers,[6] we wanted to determine how general such a pyrolysis reaction was and what other unsaturated compounds might undergo a similar cyclic molecular decomposition. Thus we became interested in what other atoms could be located in the six-membered ring and still have the cyclic molecular mechanism operate.

In ester pyrolysis A and C are oxygen atoms while in the Chugaev reaction, which involves the pyrolysis of a xanthate
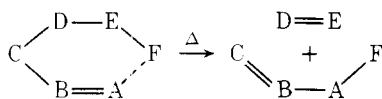
ester, a sulfur atom is located in position A. Similarly, previous work in these laboratories showed that pyrolysis of amides,[7,8] in which C is a nitrogen atom, occurs by the same cyclic mechanism but involves a temperature that is at least 60 °C higher than that required for ester pyrolysis. More recently, a study of the pyrolysis of vinyl ethers[1] in which A is a carbon atom showed that these materials pyrolyze at a temperature 40–50 °C lower than the temperature necessary for comparable ester pyrolysis. The ease of pyrolysis of various compounds can be rationalized by the assumption that the transition state in the cyclic mechanism looks more like the products than the starting materials, and that if a stable double bond between A and B is converted to a less stable double bond between C and B, a higher temperature is required for pyrolysis than is necessary for the pyrolysis of the symmetrical ester. Conversely, if a high-energy double bond between A and B is converted to a more stable double bond between C and B in the products, a temperature lower than that required for the pyrolysis of the symmetrical ester group is noted.

In such a system a ketone which has a carbon atom in position C and oxygen in position A is a counterpart to the vinyl ether which has the oxygen in position C and a carbon in position A. For this reason it was of interest to study the pyrolysis of ketones in order to see if the relationship discussed above is followed and that ketones do indeed pyrolyze by a cyclic six-membered mechanism and require temperatures considerably higher than those required for ester pyrolysis.

Although there are many examples in the literature of the photolysis of ketones,[9–12] little work has been done on the pyrolysis of ketones. Methyl n-propyl ketone is one ketone for which both photolysis and pyrolysis data are available. However, because of the lack of uniformity in pyrolysis and photolysis conditions, the results are hard to compare. McNesby and Gordon[13] reported that the pyrolysis and photolysis of 2-pentanone-1,1,1,3,3,-d_5 gave more acetone-d_6 than acetone-d_5. If the cyclic mechanism were operative, all the acetone should have been d_5. They concluded that in the pyrolysis region the reaction appeared to involve a free-radical mechanism. However, Ausloos and Murod[14] studied the photolysis of 2-pentanone-1,1,1,3,3-d_5 and reported that 90% of the acetone obtained was acetone-d_5. They concluded that the intermolecular cleavage through a six-membered ring was operating.

Guenther[15] reported the formation of large quantities of methyl vinyl ketone plus some acetone from the gas-phase thermal decomposition of methyl n-propyl ketone at 500–530 °C. Waring and Garik[16] pyrolyzed methyl n-propyl ketone and concluded that it decomposed predominately through a free-radical mechanism. Blades and Sandhu[17] reported that at 652 °C methyl n-propyl ketone undergoes almost no decomposition but produced minor amounts of methane, ethylene, and acetone. They also reported that the rate constant for acetone formation was 0.016 s^{-1} with an Arrhenius factor of 59. Furukawa and Naruchi[18] pyrolyzed methyl n-propyl ketone at 500 °C over calcium carbonate to yield acetone plus di-n-propyl ketone.

In 1957, Walters and Barry[19] studied the gas-phase thermal decomposition of methyl n-butyl ketone from 430 to 500 °C. The principal products of the reaction during early stages of the reaction are (1) propylene and acetone, (2) ethane and methyl vinyl ketone, and (3) methane, carbon monoxide, and 1-butene. Since methane and carbon monoxide grow in importance during the decomposition, they are probably formed by the decomposition of intermediate products. Waring et al.[20–22] studied the decomposition of acetone, methyl ethyl ketone, and diethyl ketone and concluded that all three decomposed primarily through a free-radical chain mechanism. Skraup and Guggenheim[23] reported that the products from heating dibenzoylpropane for 20 h at 330 °C in a bomb were acetophenone and phenyl vinyl ketone. Although the authors did not postulate a mechanism, the products can be rationalized on the basis of a cyclic mechanism. Finally, Allan, McGee, and Ritchie[24] studied the pyrolysis of acetylacetone at 500 °C and reported the production of acetone, ketene, and isopropenyl acetate, plus some methylacetylene, ethylene, and methane. Blades and Sandhu[17] also reported that acetylace-

tone gave acetone when heated at 505 °C, but they did not detect the expected ketene. Thus, although there are fairly extensive data in the literature on the photolysis and pyrolysis of ketones, there has been no systematic study that would allow direct comparison with ester pyrolysis and apparently no attempt has been made to maximize the yield of products from the pyrolysis of ketones. We therefore undertook the study of several acyclic ketones by conducting the pyrolysis in the same apparatus and under conditions that were comparable to those used for the pyrolysis of esters.

Heptane-2,6-dione was selected for the initial studies since the compound was symmetrical and contained activated γ-hydrogen atoms. The procedure of Cope, Dryden, Overberger, and D'Addieco[25] was used to synthesize the heptane-2,6-dione dioxime and the method of Overberger et al.[26] was used to convert the dioxime to the dione in a 42% yield. Pyrolysis at 650 °C gave a 22% yield of acetone and a 17% yield of methyl vinyl ketone, together with a 66% recovery of the diketone. The yields of acetone and methyl vinyl ketone, based on unrecovered starting material, were 61 and 45%, respectively.

A modification of the procedure of Mosher and Cox[27] was used to prepare methyl neopentyl ketone by the oxidation of technical grade diisobutylene with potassium dichromate in an overall yield of 47%. Pyrolysis of the methyl neopentyl ketone at 690–695 °C gave a 17% yield of acetone and an 18% yield of isobutylene together with a 61% recovery of the starting ketone. The yields of acetone and isobutylene (based

on unrecovered starting material) were, therefore, 44 and 46%, respectively. At 500 °C, a temperature at which *tert*-butyl acetate is essentially completely pyrolyzed to isobutylene and acetic acid, the methyl neopentyl ketone is recovered unchanged. In a very similar manner 4-methyl-2-pentanone was pyrolyzed at 665 °C to produce in the following yields: propylene (10%), acetone (7%), and recovery of the starting ketone (75%); in addition an 8% yield of isobutylene was obtained. The yields of acetone and propylene, based on unrecovered starting material, were 28 and 40%, respectively. The extent of decomposition appears to be somewhat less than in the case of the heptane-2,6-dione or the methyl neopentyl ketone.

Methyl *n*-propyl ketone proved to be more thermally stable than the more highly substituted ketones previously discussed. Pyrolysis of methyl *n*-propyl ketone at 650 °C gave an 87% recovery of starting material plus a 6% conversion to acetone and a 3% conversion to ethylene, both products expected from the operation of the cyclic mechanism. However, there also was obtained a 5% conversion to methyl vinyl ketone, the formation of which can be rationalized by the operation of a free-radical chain reaction involving the abstraction of the α-hydrogen atom. Finally, for comparison acetone was treated at 650 °C under the conditions used for the pyrolysis of methyl *n*-propyl ketone; the acetone was recovered unchanged and no indication of decomposition was noted.

Thus, it appears that ketones are considerably more thermally stable than esters, requiring some 150 °C higher temperature for a comparable extent of decomposition. This is in marked contrast to the vinyl ethers,[1] which require a temperature some 40–50 °C lower than that required for a comparable degree of pyrolysis of an ester. The data from the pyrolysis of the ketones support the concept that the transition state for the cyclic six-membered mechanism resembles the products more than it does the starting materials.

The process of changing from a relatively stable carbon–oxygen double bond in the starting ketone to the less stable, higher energy carbon-to-carbon double bond character in the transition state requires a higher temperature for operation. The introduction of a quaternary carbon in the starting ketone tends to promote the thermal decomposition in order to relieve some of the strain. Similarly, the introduction of a second carbonyl group, as in heptane-2,6-dione, not only activates the hydrogen atom by reducing its bond strength but also stablizes the double bond character in the transition state.

Since the pyrolysis of ketones required such high temperatures, the reactions are not as clean as the pyrolysis of esters. The cleavage takes place at temperatures at which competing reactions, usually free-radical reactions, also occur. The formation of many of the by-products usually can be rationalized by the operation of radical chain reactions. In other words, these pyrolyses undoubtedly represent a competition between the concerted retro-ene reaction and homolytic bond breaking processes. Thus it appears that the pyrolysis of ketones will be of synthetic utility only for those ketones that have some degree of internal strain to promote decomposition or that contain some group that will stabilize the products.

Experimental Section[28]

Pyrolysis of 2,6-Heptanedione. An adaptation of procedures which appear in the literature[25,26] was used to synthesize the 2,6-heptanedione. From 478 g (4.46 mol) of 2,6-dimethylpyridine, 1850

mL of anhydrous methanol, 103 g (4.46 g-atoms) of sodium, and 335 g (4.83 mol) of hydroxylamine hydrochloride in 600 mL of 50% ethanol was obtained 47.4 g (46% yield based on sodium) of 2,6-heptanedione dioxime, mp 79–82 °C (reported[26] mp 83.4–84.6 °C). When 10.5 g (0.66 mol) of 2,6-heptanedione dioxime dissolved in 115 mL of 10% aqueous sulfuric acid was treated with a solution of 9.2 g (0.132 mol) of sodium nitrite in 15 mL of water, 3.5 g (42%) of 2,6-heptanedione, bp 48 °C (0.5 mm), mp 31–33 °C (reported[26] bp 48–50 °C (1.0 mm), mp 31–33 °C), was obtained.

A Hoskins Type FD303-A electric furnace, permanently clamped in a vertical position in a rack and equipped with an iron–constantan thermocouple and a potentiometrically calibrated pyrometer, was fitted with a 1 × 20 in. Vycor tube fitted with a standard taper $^{24}/_{40}$ outer joint at the top, a $^1/_4$ × 2 in. side-inlet tube near the top, and a standard-taper $^{24}/_{40}$ inner joint at the bottom, and packed to a depth of about 6.5 in. with Vycor chips. An inert atmosphere was maintained in the pyrolysis tube by the introduction of a slow stream of dry oxygen-free nitrogen. The pyrolysate was initially cooled by a 6-in. water-cooled spiral condenser and collected in a 5.5-in. test tube immersed in a dry ice–methyl Cellosolve bath. Attached between the condenser and the test tube by means of $^{24}/_{40}$ standard-taper joints was a two-way connecting tube with a side-arm suction tube. The material which did not condense in the test tube passed through the connecting tube into two condenser traps immersed in a dry ice–methyl Cellosolve bath and then into a tube containing a solution of bromine in carbon tetrachloride.

The 2,6-heptanedione (3.5 g) to be pyrolyzed was placed in a 10-mL separatory funnel and the ketone was dropped through the pyrolysis tube heated at 650 °C at the rate of 20 drops/min, while the tube was flushed with dry oxygen-free nitrogen (90 bubbles/min) to minimize oxidation and charring. Examination of the tube after pyrolysis indicated very little charring had taken place. The water-white pyrolysate which was collected amounted to 2.6 g. Weighed amounts of benzene and 2-octanone were added to the pyrolysate to serve as internal standards for the chromatographic analysis of the mixture. Known mixtures of benzene with acetone and methyl vinyl ketone as well as known mixtures of 2-octanone and 2,6-heptanedione were calibrated with regard to retention times and quantitative area responses. From a chromatographic analysis of the pyrolysate, it was shown to contain acetone (22%), methyl vinyl ketone (17%), and 2,6-heptanedione (66%). The yield of acetone and methyl vinyl ketone, based on unrecovered starting diketone, was 61 and 45%, respectively. No other products were found in the pyrolysate or in the bromine–carbon tetrachloride trap. When pyrolyses were attempted at 570 and 625 °C, little or no cleavage occurred.

Pyrolysis of Methyl Neopentyl Ketone. A modification of the procedure of Mosher and Cox[27] was used to prepare methyl neopentyl ketone. In a 5-L three-necked flask equipped with a mechanical steel stirrer, a dropping funnel, and a reflux condenser were placed 1179.6 g (4 mol) of potassium dichromate and 800 mL of water. To the reaction mixture was added 336.6 g (3 mol) of technical diisobutylene (80% 2,4,4-trimethyl-1-pentene), bp 101–103 °C, $n^{25}{}_D$ 1.4067 (reported[27] bp 101–104 °C, $n^{25}{}_D$ 1.4060), followed by the addition of 1569 g (16 mol) of concentrated sulfuric acid with vigorous stirring over a period of 5 days. The temperature of the reaction mixture was maintained at 25–30 °C by the rate of addition of sulfuric acid, and then stirring was continued for an additional day. After steam distillation of the reaction mixture and drying of the distillate over magnesium sulfate, 240.5 g of crude methyl neopentyl ketone was obtained. Careful fractionation of the crude product through a 24-in. helix-packed column yielded 128 g (47%) of methyl neopentyl ketone, bp 123–125 °C (760 mm), $n^{25}{}_D$ 1.4008 (reported[27] bp 124–125 °C, $n^{25}{}_D$ 1.4018).

Anal. Calcd for C$_7$H$_{14}$O: C, 73.62; H, 12.36. Found: C, 73.48; H, 12.28.

Chromatographic analysis of the ketone showed the presence of only one peak in the chromatogram.

When the methyl neopentyl ketone (10.3 g) was pyrolyzed at 660 °C at the rate of 22 drops/min through the apparatus described above, a water-white pyrolysate was collected and no charring occurred in the tube. A weighed amount of methyl ethyl ketone was added to the pyrolysate as an internal standard and the mixture was analyzed on a gas chromatograph as described previously. The pyrolysate was shown to contain acetone (17%), isobutylene (18%), methyl neopentyl ketone (61%), and unidentified materials (4%). The yields of acetone and isobutylene, based on unrecovered methyl neopentyl ketone, were 44 and 46%, respectively.

When the temperature of pyrolysis was 585 or 630 °C, practically no pyrolysis occurred and the starting methyl neopentyl ketone was

recovered unchanged. Also when a temperature of 690 °C was employed, much greater quantities of low-boiling "fragmentation" products, which were presumably formed by free-radical reactions, were noted. Analysis of the material in the bromine–carbon tetrachloride trap indicated that practically no material was collected.

Pyrolysis of Methyl Isobutyl Ketone. Commercial methyl isobutyl ketone (Matheson Coleman and Bell) was carefully fractionated through an 8-in. helix-packed column to give a water-white chromatographically pure distillate, bp 114–117 °C (reported[29] bp 114–116 °C). In the apparatus just described, 3.87 g of methyl isobutyl ketone was added to the pyrolysis tube heated at 650–655 °C at the rate of 60 drops/min. After a weighed amount of methyl ethyl ketone was added as an internal standard, the mixture was analyzed on a gas chromatograph to indicate that the pyrolysate consisted of some propylene, isobutylene (8%), acetone (7%), and methyl isobutyl ketone (75%). Although some of the volatile materials passed into the bromine trap, the material in the bromine–carbon tetrachloride trap was worked up in the usual way and the resulting 1,2-dibromopropane was analyzed in a gas chromatograph with a weighed amount of 1,2,3-tribromopropane added as internal standard. The analysis indicated that a 10% conversion to propylene had occurred during pyrolysis. The yields of acetone and propylene, based on unrecovered methyl isobutyl ketone, were 38 and 40%, respectively. Pyrolysis of methyl isobutyl ketone at 625 °C resulted in nearly complete recovery of starting material.

Pyrolysis of Methyl n-Propyl Ketone. Commercial methyl n-propyl ketone (Brothers Chemical Co.) was distilled through an 8-in. helix-packed column to yield a clear liquid chromatographically pure distillate, bp 100–103 °C (reported[29] bp 102 °C). In the apparatus just described 2.94 g of methyl n-propyl ketone was added at the rate of 20 drops/min to the Vycor tube heated at 650 °C with the pyrolysate being collected in a tube cooled in dry ice and the low-boiling olefins collected in a bromine–carbon tetrachloride trap. A weighed amount of benzene was added to the pyrolysate as an internal standard and the mixture was analyzed on a gas chromatograph which showed that the pryolysis gave acetone (5%), methyl vinyl ketone (4%), and recovered methyl n-propyl ketone (60%). Analysis of the bromine–carbon tetrachloride trap showed the production of ethylene (1%) and propylene (1%).

Pyrolysis of Acetone. When acetone was pyrolyzed at 650 °C in the apparatus described previously, chromatographic analysis of the pyrolysate showed only the presence of acetone in nearly a quantitative recovery.

References and Notes

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