

showed that the sample contained 3% of the exocyclic isomer.

**Methylenecyclohexane** was formed by pyrolysis of cyclohexylmethyl acetate. The infrared spectrum, which is very different from that of 1-methylcyclohexene, supported its structure.

**1-Methylcyclopentene** was prepared by oxalic acid-catalyzed dehydration of 1-methylcyclopentanol. Gas chromatograms of the product gave a single peak and the infrared spectrum showed no significant absorption in the 11.3  $\mu$  region (no =CH<sub>2</sub>), b.p. 74.8° (730 mm.), lit.<sup>32</sup> b.p. 75.1° (760 mm.).

**1,2-Dimethylcyclopentene** was prepared by dehydration of 1,2-dimethylcyclopentanol with oxalic acid. The product was fractionated to yield pure 1,2-dimethylcyclopentene, b.p. 103–104° (733 mm.), lit.<sup>33</sup> b.p. 105°.

**1,2-Dimethylcyclohexene** was prepared by iodine dehydration of 1,2-dimethylcyclohexanol. The product was fractionated, b.p. 136.0–136.1° (735 mm.), lit.<sup>7</sup> b.p. 136.2°. Its infrared spectrum supported its structure although G.P.C. analysis showed that it was not completely free of its isomers.

**Pyrolysis.**—Pyrolyses were carried out by dropping the liquid esters into vertically-mounted externally-heated columns at rates of 0.1–7 ml. per minute. Dry, purified nitrogen was passed slowly through the columns and the products were collected in Dry Ice traps. Two columns were used; one was a 55-cm. Vycor Tube packed to a height of 25 cm. with 1/8 inch Pyrex helices or Pyrex beads, the other was a 25-cm. Pyrex tube packed to a height of 20 cm. with 1/16 inch Pyrex helices.

(32) G. Egloff, "Physical Constants of Hydrocarbons," Vol. 2, Reinhold Publishing Corp., New York, N. Y., 1940, p. 306.

(33) G. Chiurdoglu, *Bull. soc. chim. Belg.*, **47**, 363 (1938).

**Analysis.**—The olefinic products were either distilled into a Dry Ice trap and sampled, or the pyrolysis product was sampled directly. The pyrolysis column was then washed with water and the products were diluted with pentane and washed with water. An aliquot of the combined water washes was titrated with standard sodium hydroxide to determine the amount of acetic acid liberated.

**Gas Chromatography Equipment.**—The gas chromatographic apparatus was constructed making use of a Gow-Mac thermal conductivity cell. The column used for analysis of low-boiling olefins was an 18 foot  $\times$  0.25 inch copper tube packed with dibutyl phthalate on 40–60 mesh firebrick. For the heptenes, the column used was 10 feet long and packed with dioctyl phthalate, and for the cyclic olefins a 10-foot column with Apiezon L as the liquid phase was used. Peak areas were calculated by triangulation.<sup>35</sup>

**Control Experiments.**—The lack of rearrangement of olefins under the reaction conditions was demonstrated by pyrolysis of several primary acetates. In every case such reactions gave only terminal olefins. To demonstrate that no *cis-trans* interconversion occurred, a mixture of *n*-butyl acetate and *cis*-2-butene was passed through the column. A mixture of *cis*-2-butene and 1-butene, uncontaminated by *trans*-2-butene, was formed. In a number of cases the products of a pyrolysis were passed again through the pyrolysis column. No change in olefin ratios was observed.

(34) Identical results were obtained by sampling the pyrolysate directly or distilling the olefins and sampling the olefin mixture. Consequently either technique could be used, depending upon its convenience in a particular case.

(35) A. I. M. Keulemans, "Gas Chromatography," Reinhold Publishing Corp., New York, N. Y., 1957, p. 32.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MARYLAND]

## Pyrolysis of Esters. XV. Effect of Temperature on Direction of Elimination of Tertiary Esters<sup>1</sup>

BY WILLIAM J. BAILEY AND WARREN F. HALE<sup>2</sup>

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Reinvestigation of the pyrolysis of *t*-amyl acetate showed that at 400° the elimination followed the Hofmann rule, producing 74% of 2-methyl-1-butene, but at 225° the elimination followed the Saytzeff rule, producing 58% of the isomeric 2-methyl-2-butene. Pyrolysis of dimethylisopropylcarbinyl acetate at 400° gave a mixture of olefins consisting of 88% of 2,3-dimethyl-1-butene and 12% of 2,3-dimethyl-2-butene. Pyrolysis of 1-methylcyclohexyl acetate under a wide variety of conditions always produced a mixture in which the endocyclic olefin was the major product.

Since the advent of vapor-phase chromatography has made the analysis of liquids comparatively easy, a study of the factors influencing the direction of elimination during the pyrolysis of esters was initiated. This study was further undertaken because recent work in this Laboratory<sup>3</sup> had shown that the pyrolyses of amides were not as selective as had been reported originally for esters.<sup>4</sup> It was reported earlier that the pyrolyses of tertiary esters followed the Hofmann rule, producing, as the major product, the least highly alkylated olefin with very little of the other possible isomer. For instance, the pyrolysis of *t*-amyl acetate (I) at 400° was reported to yield mostly 2-methyl-1-butene (III). This conclusion was based on the comparison of the physical properties of the pyrolysis product with those reported in the literature for the two possible

products. When the pyrolysis of a related *t*-alkyl amide produced a mixture of the two possible olefins, the pyrolysis of *t*-amyl acetate was reinvestigated.

In the first phase of this study the pyrolyses were conducted over a wide temperature range (250–600°) with a packing of Pyrex helices in the pyrolysis tube. In each case no attempt was made to separate the pyrolysate, but a sample was introduced directly into a vapor-phase chromatography column to determine the relative amounts of the olefinic products. The results of this temperature study are listed in Table I. From this study it appears that, although the pyrolyses at the higher temperatures follow the Hofmann rule in producing as high as 74% of the 2-methyl-1-butene (III), the selectivity is not as high as originally thought. It is highly significant that at the lower temperatures the elimination follows the Saytzeff rule, producing 58% of the 2-methyl-2-butene (II). This last result suggests that liquid-phase pyrolyses would be more apt to follow the Saytzeff rule than

(1) Previous paper in this series, *J. Org. Chem.*, **22**, 1002 (1958).

(2) Office of Naval Research Fellow, 1955–1956; Union Carbide Fellow, 1956–1957.

(3) W. J. Bailey and C. N. Bird, *J. Org. Chem.*, **22**, 996 (1958).

(4) W. J. Bailey, J. J. Hewitt and C. King, *THIS JOURNAL*, **77**, 357 (1955).

would vapor-phase pyrolyses. Thus one could account for many of the apparent discrepancies between vapor and liquid phase pyrolyses on this basis. In fact, Barton<sup>5</sup> concluded, mostly on the basis of liquid-phase pyrolyses, that the Saytzeff rule was followed quite generally. This result also suggests that the stability of the olefin becomes an increasingly more important factor as the temperature of pyrolysis is lowered. Of course, at the present time the possibility can not be ruled out that the mechanism of the reaction is shifting from a cyclic intermediate to involve ionic intermediates.

TABLE I  
EFFECT OF TEMPERATURE ON PYROLYSATE FROM *t*-AMYL ACETATE (I)

Temp., °C.	Olefin, %	
	2-Methyl-1-butene (III)	2-Methyl-2-butene (II)
225	42	58
275	45	55
350	54	46
400	70	30
500	69	31
600	55 <sup>a</sup>	30 <sup>a</sup>

<sup>a</sup> Plus 15% 3-methyl-1-butene.

In an effort to find experimental conditions that would produce a higher selectivity, a series of pyrolyses were performed with a variety of packing materials and methods of addition. The results are summarized in Table II. It made little difference in the composition of the pyrolysate whether the packing was soft glass or Vycor or whether the packing was cleaned with nitric acid or washed with a base. It also made little difference whether the packing was glass beads or glass wool. Only a very small increase in the 2-olefin II was noted when the packing was coated with a heavy carbon deposit. It had been noted previously many times that conditions that promoted carbonization often produced rearrangements.<sup>6</sup> However, it was extremely difficult to produce any carbonaceous material from *t*-amyl acetate. Even at 600° little charring occurred, even though the pyrolysate contained 15% of 3-methyl-1-butene. Even though conditions were violent enough to promote some rearrangement of the double bond, the ratio of the other two olefins remained essentially constant. It is difficult to rationalize the formation of the 3-methyl isomer without the assumption of the existence of an intermediate carbonium ion.

In a similar study, dimethylisopropylcarbinyl acetate (IV) was pyrolyzed at 400° to yield, as the major product, 2,3-dimethyl-1-butene (V), according to the Hofmann rule. However, even in this case the selectivity was not as high as originally thought with the pyrolysate containing only 88% of the 1-olefin V and 12% of the isomeric 2,3-dimethyl-2-butene (VI).

Since these examples did not indicate the selectivity previously reported, the pyrolysis of 1-methylcyclohexyl acetate (VII) was also reinvestigated.<sup>4</sup> This ester was ideal for this study since the two possible olefins differ considerably in

stability and the previous results have been confirmed in several other laboratories. For these reasons 1-methylcyclohexyl acetate (VII) was pyrolyzed over a temperature range from 220 to 550°, as indicated in Table III. It was indeed surprising that the major component in all cases was the *endo* isomer. In fact, the highest amount of the methylenecyclohexane (IX) obtained in any pyrolysis was less than 30%. The same effect of temperature on the composition of the olefins is noted, however, that was found in the pyrolysis of *t*-amyl acetate, but the variation is over a much narrower range of compositions.

TABLE II  
EFFECT OF PACKING ON PYROLYSATE FROM *t*-AMYL ACETATE AT 400°

Packing	Olefin, %	
	2-Methyl-1-butene (III)	2-Methyl-2-butene (II)
Pyrex helices	70	30
Pyrex glass wool	74	26
Vycor chips	74	26
Soft glass beads	71	29
Pyrex helices charred with:		
Isopropenyl acetate	75	25
Ethyl benzoylacetoacetate	71	29
2,3-Dicarbomethoxy-2,3-diacetoxy-butane	74	26

TABLE III  
EFFECT OF TEMPERATURE ON PYROLYSATE FROM 1-METHYL-CYCLOHEXYL ACETATE (VII)

Temp., °C.	Composition of pyrolysate, %	
	Methylene-cyclohexane (IX)	1-Methylcyclohexene (VIII)
220 <sup>a</sup>	17	83
300	15	85
400	18	82
450	26	74
550	26	74

<sup>a</sup> Liquid-phase pyrolysis (bath temp.)

Since these results were in marked contrast to our previous results, we would normally assume that there was some error in our previous work. In that study we isolated the olefin from the pyrolysate and showed that its infrared spectrum was very similar to that of an authentic sample of methylenecyclohexane (IX) prepared from a pyrolysis of cyclohexylcarbinyl acetate (X). In the present work the composition of the pyrolysate was determined by direct vapor-phase chromatography as well as interpolation of the infrared curves of known mixtures of the two olefins. The methylenecyclohexane (IX) from pyrolysis of the primary acetate was shown by vapor-phase analysis to be at least 99% pure while the 1-methylcyclohexene (VIII), prepared by the dehydration of 1-methylcyclohexanol (XI) with iodine,<sup>7</sup> was 98.7% pure with only 1.3% of the *exo* isomer as a contaminant. However, in view of the independent confirmation of our earlier work, one can speculate that we were not duplicating the previous experimental conditions.

(5) D. H. R. Barton, *J. Chem. Soc.*, 2174 (1946).

(6) W. J. Bailey and J. Rosenberg, *THIS JOURNAL*, **77**, 73 (1955).

(7) P. D. Bartlett and R. H. Rosenwald, *ibid.*, **56**, 1993 (1934).

The most convincing confirmation of the formation of the methylenecyclohexene (IX) from the pyrolysis of the tertiary acetate VII is the recent work of Traynham and Pascual.<sup>8</sup> Their evidence, in addition to physical properties and infrared spectra, included the formation of several derivatives. The olefin from the pyrolysate reacted with peroxyformic acid to give a 52% yield of a solid glycol (which gave an 81% yield of cyclohexanecarboxaldehyde with hydrobromic acid) and reacted with hypobromous acid<sup>9</sup> to give an 87% yield of 1-bromomethylcyclohexanol (which was synthesized independently from cyclohexanone and diazomethane, followed by treatment of the intermediate epoxide with hydrogen bromide). A similar reaction with hypochlorous acid gave a 67% yield of the corresponding 1-chloro tertiary alcohol. Their infrared data were less clear-cut since they state, "small differences in position and relative intensities of the infrared absorption bands distinguish the spectra" of the two olefins. In the present work many strong bands were present in one isomer but not in the other.

Siegel and Dunkel<sup>10</sup> reported in a study of the pyrolyses of 1,2-,1,3- and 1,4-dimethylcyclohexyl acetates difficulty in obtaining the high selectivity that we originally reported.<sup>4</sup> However, they were able to obtain high selectivity to produce the pure *exo* isomer in each case if the proper experimental conditions were used. Nevitt and Hammond<sup>11</sup> found that the pyrolysis of 1-methylcyclohexyl acetate (VII) gave 86% of the *exo* isomer IX and 14% of the *endo* isomer VIII, based on a graphical interpolation of infrared data. [Unfortunately, the bands at 833 and 1110 wave numbers in the pure *exo* isomer used for the calculations were not found in solution spectrum of our sample of methylenecyclohexane (IX).] The pyrolysis of *trans*-1,2-dimethylenecyclohexyl acetate gave a mixture containing 90% of 2-methylmethylenecyclohexane, while the pyrolysis of the corresponding *cis* ester gave 89% of the same isomer. Brenner and Schinz<sup>12</sup> obtained a 52% yield of cyclolavandulol, which is a 3,5-disubstituted methylenecyclohexane, by the liquid-phase pyrolysis of the corresponding tertiary acetate.

In order to try to find the reason for this obvious discrepancy between our present results and those previously reported, a large number of pyrolyses of 1-methylcyclohexyl acetate (VII) were performed under a variety of special conditions, as listed in Tables III and IV. It did not appear to make any great difference whether new Pyrex helices were washed with an excess of bicarbonate solution or cleaned with nitric acid. It also did not make any appreciable difference whether the ester was diluted with pyridine or acetic acid. Even

(8) J. G. Traynham and O. S. Pascual, *J. Org. Chem.*, **21**, 1362 (1956).

(9) J. G. Traynham and O. S. Pascual, Abstract of Papers, 131st Meeting of the American Chemical Society, Miami, Fla., April, 1957, p. 45-O.

(10) S. Siegel and M. Dunkel, Abstracts of 129th National Meeting of the American Chemical Society, Dallas, Texas, April 8-13, 1956, p. 28-N.

(11) T. D. Nevitt and G. S. Hammond, *THIS JOURNAL*, **76**, 4124 (1954).

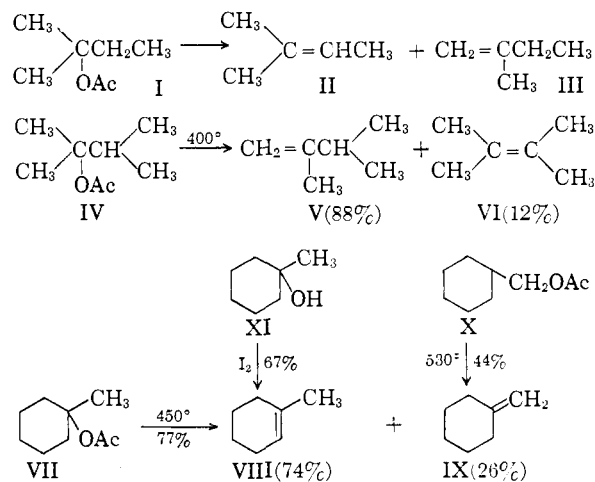
(12) A. Brenner and H. Schinz, *Helv. Chim. Acta*, **35**, 1333 (1952).

TABLE IV

EFFECT OF CONDITIONS ON PYROLYSATE FROM 1-METHYLCYCLOHEXYL ACETATE (VII) AT 450° OVER PYREX HELICES

Special conditions	Composition of pyrolysate, %	
	Methylene-cyclohexane (IX)	1-Methylcyclohexene (VIII)
New helices washed with base	29	71
Helices coated with carbon	26	74
Three pyrolyses through same tube	26	74
Ester containing:		
Excess acetic acid	25	75
5% pyridine	23	77
150% pyridine	22	78
1% benzoyl peroxide	26	74
4% azo catalyst	24	76
5% hydroquinone	28	72

the size of the run made no significant difference. In order to eliminate the possibility that free radicals were playing some role in the decomposition, several runs were made with ester containing benzoyl peroxide or an azobisnitrile. Similarly, the addition of 5% hydroquinone had little effect. As expected, the method of preparation of VII had no effect.



These results also do not parallel the results of amine oxide decomposition. Cope, Bumgardner and Schweizer,<sup>13</sup> as well as Baumgarten, Bower and Okamoto,<sup>14</sup> found that the decomposition of the corresponding 1-methylcyclohexyl amine oxide gave at least 97% of methylenecyclohexane (IX). Although the amine oxides apparently decompose by a cyclic transition state similar to that occurring in ester pyrolysis, the intermediate ring involves only five atoms instead of six. This might lead one to expect different results from the two reactions in some cyclic systems. It does appear that ester pyrolysis does parallel amine oxide pyrolysis in one respect. Cope, LeBel, Lee and Moore<sup>15</sup> found that in the aliphatic compounds the amine oxides formed a ratio of olefins roughly parallel to the ratio of available  $\beta$ -hydrogens. The present

(13) A. C. Cope, C. L. Bumgardner and E. E. Schweizer, *THIS JOURNAL*, **79**, 4729 (1957).

(14) H. E. Baumgarten, F. A. Bower and T. T. Okamoto, *ibid.*, **79**, 3145 (1957).

(15) A. C. Cope, N. A. LeBel, H. Lee and W. R. Moore, *ibid.*, **79**, 4720 (1957).

study tends to indicate that ester pyrolysis may also follow this rule.

One could conclude that there are possible at least two sets of experimental conditions for the pyrolysis of esters which give slightly different results in the direction of elimination. One set of conditions appears to give the exocyclic isomer and to proceed in a selective manner according to the Hofmann rule. These highly elusive conditions, however, are not the normal operating conditions and at the present time can not be defined. Under normal operating conditions the elimination in simple aliphatic compounds tends to follow the Hofmann rule to give a mixture of olefins roughly in the same ratio as the number of available hydrogens. Low temperatures of pyrolysis tend to favor the Saytzeff product. The relative stabilities of the olefins must play a role, since the pyrolysis of cyclohexyl tertiary ester tends to give primarily the more stable endocyclic isomer.

### Experimental<sup>16</sup>

**Pyrolysis of *t*-Amyl Acetate (I).**—*t*-Amyl acetate was fractionated through a 24-inch, helix-packed column to yield relatively pure ester, b.p. 122.5–123.5° (758 mm.),  $n_D^{25}$  1.3965 [reported<sup>4</sup> b.p. 62–64° (97 mm.),  $n_D^{20}$  1.3980]. The ester was pyrolyzed under a variety of conditions and the results are summarized in Tables I and II. The apparatus, which consisted essentially of a Vycor tube packed with Pyrex helices (unless otherwise indicated) and externally heated with a 12-inch Hoskins furnace, has been described in detail.<sup>17</sup> In a typical pyrolysis, 16.0 g. (0.12 mole) of *t*-amyl acetate (I) was added dropwise at the rate of 1 g. per minute to the top of the pyrolysis tube heated at 400°. At the end of the pyrolysis, a small sample of the pyrolysate was immediately analyzed on the vapor-phase chromatograph and from the areas under the curve it was calculated that the mixture of olefins consisted of 70% of 2-methyl-1-butene (III) and 30% of 2-methyl-2-butene (II). After the pyrolysate had been washed with water until it was neutral, the aqueous extracts were titrated with standard base to indicate that 77% of the theoretical amount of acetic acid had been liberated. In all cases the two isomeric olefins II and III were resolved on the "A" column of the Perkin-Elmer vapor fractometer model 154 at 27°, helium pressure 20 pounds, detector voltage at 4 volts, and sensitivity four. The peaks were identified by comparison with the retention times of authentic samples. A sample of 2-methyl-1-butene (III) was available from Phillips Petroleum Co. and the 2-methyl-2-butene (II) was prepared by the fractionation of the dehydration product of *t*-amyl alcohol.<sup>18</sup> [The pyrolysis of methylisopropylcarbinyl acetate produced, in addition to the major product, 3-methyl-1-butene, a small amount of an olefin having the same retention time as the olefin assumed to be 2-methyl-2-butene (II).] The sample of 3-methyl-1-butene was available from the pyrolysis of isoamyl acetate.<sup>19</sup> Unless indicated, no charring was noted in any of the pyrolysis tubes. In one run at 400° the acetate I was distilled into the pyrolysis tube, but the results indicated that the pyrolysate contained 67% of 2-methyl-1-butene (III) and 33% of 2-methyl-2-butene (II).

**Pyrolysis of Dimethylisopropylcarbinyl Acetate (IV).**—A sample of this ester<sup>4</sup> was redistilled through a 6-inch, helix-packed column to yield fairly pure dimethylisopropylcarbinyl acetate (IV), b.p. 79–80° (90 mm.),  $n_D^{25}$  1.4068 [reported<sup>4</sup> b.p. 73° (80 mm.),  $n_D^{25}$  1.4052]. At the rate of 1.0 g. per minute, 4.4 g. (0.031 mole) of IV was pyrolyzed at 400° as previously described with no carbonization occur-

ring in the tube. Vapor-phase analysis of the pyrolysate indicated that the olefins consisted of 88% of 2,3-dimethyl-1-butene (V) and 12% of 2,3-dimethyl-2-butene (VI). Good resolution of the two isomers was obtained on "A" column described above at 40°. Under these conditions V had a retention time of 7 minutes and VI of 14 minutes. The pyrolysate, which was washed free of acetic acid with water, was diluted with 10 ml. of *n*-pentane. (Titration of an aliquot of the aqueous extracts indicated that 87% of the theoretical amount of acetic acid had been liberated.) Infrared absorption indicated very strong methylene peaks at 895 and 1650  $\text{cm}^{-1}$ , but only very weak tetrasubstituted double bond peaks at 820 and 960  $\text{cm}^{-1}$ .

**1-Methylcyclohexyl acetate (VII).** A. By Acetic Anhydride-Magnesium Method.—Cyclohexanone was converted to 1-methylcyclohexanol, b.p. 66–68° (25 mm.),  $n_D^{25}$  1.4590 (reported<sup>11</sup> b.p. 68° (24 mm.),  $n_D^{25}$  1.4582), in a 74% yield by reaction with methylmagnesium iodide. A vapor-phase chromatogram indicated that this sample was at least 98% pure. A mixture of 456 g. (4.0 moles) of 1-methylcyclohexanol, 108 g. (4.5 moles) of powdered magnesium and 1000 g. of acetic anhydride was heated under reflux for 3 days until practically all of the magnesium had reacted. The reaction mixture was poured onto ice and the resulting solution was neutralized with sodium carbonate. After the organic layer had been dried over anhydrous sodium carbonate, it was fractionated through a 12-inch, helix-packed column to yield 499 g. (80%) of 1-methylcyclohexyl acetate (VII), b.p. 172–177° (759 mm.),  $n_D^{25}$  1.4372 [reported<sup>4</sup> b.p. 177–178° (740 mm.),  $n_D^{25}$  1.4355]. This procedure has the advantage that the magnesium acts as an indicator so the reaction can be followed.

B. By Acetyl Chloride-Pyridine Method.—The procedure of Traynham and Pascual<sup>9</sup> for the esterification of 1-methylcyclohexanol with acetyl chloride and pyridine gave a 77% yield of 1-methylcyclohexyl acetate (VII), b.p. 118–118.5° (110 mm.),  $n_D^{25}$  1.4382. A vapor-phase chromatogram of this VII showed the absence of impurities.

*Anal.* Calcd. for  $\text{C}_9\text{H}_{16}\text{O}_2$ : C, 69.20; H, 10.33. Found: C, 69.24; H, 10.31.

**Pyrolysis of 1-Methylcyclohexyl Acetate (VII).**—By use of the procedure and apparatus described above, 1-methylcyclohexyl acetate (VII) was pyrolyzed under a wide variety of conditions and the results are summarized in Tables III and IV. In a typical experiment, 42.7 g. (0.27 mole) of VII was pyrolyzed at 450° by dropwise addition to the pyrolysis tube at the rate of 0.5 g. per minute. No charring on the helices was noted. After the pyrolysate had been washed with water until it was free of acid, the organic layer was dried over a mixture of magnesium sulfate and sodium carbonate. (Titration of an aliquot of the aqueous washings indicated that 94% of the theoretical amount of acetic acid had been liberated.) The organic layer was then fractionally distilled through a 6-inch, helix-packed column to yield 20.2 g. (77%) of a mixture of olefins, b.p. 106.8–108° (761 mm.),  $n_D^{25}$  1.4481. Vapor-phase chromatography indicated that this mixture consisted of 74% of 1-methylcyclohexene (VIII) and 26% of methylenecyclohexene (IX). On the "A" column described above the mixture was resolved at 73° with the other settings remaining the same. The peaks were identified by comparison of their retention times with those of authentic samples. Dehydration of 1-methylcyclohexanol was accomplished by the method of Bartlett and Rosenwald.<sup>1</sup> Fractional distillation of the crude product through a 6-inch, helix-packed column gave a 67% yield of fairly pure 1-methylcyclohexene (VIII), b.p. 109.7–110° (757 mm.),  $n_D^{25}$  1.4482 [reported<sup>7</sup> b.p. 109–109.5°,  $n_D^{20}$  1.4503]. Gas chromatography indicated the presence of 1.3% of methylenecyclohexene (IX) in this sample of VIII.

A sample of cyclohexylcarbinyl acetate (X), which was available from previous work,<sup>4</sup> was pyrolyzed at 530° as previously described. The pyrolysate, after it had been washed and dried as usual, was fractionally distilled through a 6-inch, helix-packed column to give a 29% conversion (or a 44% yield based on unrecovered material) of nearly pure methylenecyclohexene (IX), b.p. 78–78.5° (610 mm.),  $n_D^{25}$  1.4483 [reported<sup>4</sup> b.p. 100–101° (730 mm.),  $n_D^{25}$  1.4484]. (Titration of the aqueous washings indicated that 51% of the theoretical amount of acetic acid had been liberated.) A gas chromatogram indicated that this sample of IX was 99.0% pure with a 1.0% impurity of VIII.

Confirmatory evidence for the composition of the olefin mixtures was obtained from graphical interpolations of the

(16) The authors are indebted to Kathryn Gerdeman for the microanalysis. They are further indebted to Dr. E. R. Lippincott, Dr. R. A. Schroeder, Dr. A. Leifer, C. E. White, J. E. Katon and R. E. Welsh for the infrared spectra and aid in their interpretation. The infrared spectra were determined on carbon disulfide solutions in a Beckman IR-4 infrared spectrophotometer.

(17) W. J. Bailey and J. J. Hewitt, *J. Org. Chem.*, **21**, 543 (1956).

(18) The authors are indebted to Richard Mayer for this sample.

(19) W. J. Bailey and C. King, *THIS JOURNAL*, **77**, 75 (1955).

infrared absorption spectra compared to standard mixtures of VIII and IX. The values obtained by this method were always within 8% of the values obtained by use of the vapor-phase chromatograph. The vapor-phase procedure also was calibrated with several synthetic mixtures of VIII and IX. Values obtained for these synthetic mixtures were always within 4% of the calculated value and usually within 2%.

**Acknowledgment.**—The authors are indebted for discussions during the course of this work to C. H. De Puy, who has carried out a somewhat related study.

(20) C. H. De Puy, *et al.*, *J. Org. Chem.*, in press.

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## Pyrolysis of Esters. XVI. Effect of Ring Size on Formation of Alicyclic Olefins<sup>1</sup>

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Pyrolysis of 1-methylcyclopentyl acetate at 450° produced a mixture of olefins containing 84% of 1-methylcyclopentene and 16% of methylenecyclopentane. Similarly, pyrolysis of 1-methylcycloheptyl acetate at 440° gave a mixture containing 76% of 1-methylcycloheptene and 24% of methylenecycloheptane. Pyrolysis of N-(1-methylcyclohexyl)-acetamide at 570° produced a mixture containing 72% of 1-methylcyclohexene and 28% of methylenecyclohexane. In contrast to the pyrolysis of the corresponding amine oxides, the pyrolysis of esters shows no large effect of ring size on the compositions of the pyrolysates.

In a previous paper<sup>1</sup> it was shown that under usual operating conditions the pyrolysis of 1-methylcyclohexyl acetate gave a mixture of olefins containing 76% of the *endo* isomer, 1-methylcyclohexene, in contrast to work previously reported. In order to determine whether this formation of the *endo* isomer under ordinary pyrolysis conditions was general, the effect of ring size on the direction of elimination of the tertiary esters was investigated. Cope, Bumgardner and Schweizer had carried out a similar study with the corresponding amine oxides, which are thought to decompose by a mechanism similar to that proposed for ester pyrolysis.<sup>3</sup> Their results showed that the five-, six- and seven-membered tertiary cycloalkylamine oxides gave 95.5, 2.8 and 84.8% of the corresponding endocyclic isomers, respectively. The large effect of the size of the ring was quite remarkable. Traynham and Pascual<sup>4,5</sup> have reported that the pyrolyses of 1-methylcyclopentyl and 1-methylcycloheptyl acetates (II and VII) (under the same conditions that 1-methylcyclohexyl acetate was reported to give only methylenecyclohexane) gave only the exocyclic isomers. They did not report any direct evidence to indicate the purity of their product, but the chemical reactions performed on the olefins left little doubt that at least the major component was the *exo* isomer. Thus the photochemical addition of hydrogen bromide to the products of the pyrolyses gave a 60% yield of cyclopentylmethyl bromide and a 61% yield of cycloheptylmethyl bromide, respectively. Similarly, the addition of hypochlorous acid to the pyrolysis product in the five-membered series gave a 58% yield of the 1-chloromethylcyclopentanol and to that from the

seven-membered series a 64% yield of 1-chloromethylcycloheptanol. However, since we were not able to duplicate either their results or our previous results in the cyclohexyl series, it was of interest to reinvestigate these reactions.

For our studies 1-methylcyclopentyl acetate (II) was prepared by two different routes. This ester was prepared by the esterification of 1-methylcyclopentanol (I) with pyridine and acetyl chloride as well as with acetic anhydride and magnesium. Pyrolysis of either sample of the tertiary ester II at 450° gave a 63% yield of a mixture of olefins, which was shown by vapor-phase chromatography and infrared analysis to consist of 84% of 1-methylcyclopentene (III) and 16% of methylenecyclopentane (IV). As reference compounds, authentic samples of these two isomeric olefins were prepared independently. Methylenecyclopentane (IV) was prepared in a five-step synthesis starting from 1,1-dicarbethoxycyclopentane in an over-all yield of 34%. Hydrolysis of the diester gave a 96% yield of the corresponding dicarboxylic acid, which was decarboxylated to cyclopentanecarboxylic acid. Reduction with lithium aluminum hydride gave a 76% yield of the corresponding primary alcohol which was, in turn, esterified with acetic anhydride to give cyclopentylmethyl acetate (V) in a 91% yield. Pyrolysis of the primary acetate V at 540° gave a 54% yield of nearly pure methylenecyclopentane (IV), which was identified by infrared analysis and shown by vapor-phase chromatography to contain 2.6% of 1-methylcyclopentene (III). Although Lutz, *et al.*,<sup>6</sup> reported that the dehydration of 1-methylcyclopentanol (I) with iodine gave pure 1-methylcyclopentene (III), from this dehydration we produced a mixture containing approximately 90% of the *endo* isomer III plus 10% of methylenecyclopentane (IV). When this mixture was equilibrated in a hot mixture containing *p*-toluenesulfonic acid and glacial acetic acid, essentially pure 1-methylcyclopentene (III) was obtained.<sup>7</sup> The purity was

(1) Previous paper in this series, *THIS JOURNAL*, **81**, 647 (1959).

(2) Office of Naval Research Fellow, 1955-1956; Union Carbide Fellow, 1956-1957.

(3) A. C. Cope, C. L. Bumgardner and E. E. Schweizer, *THIS JOURNAL*, **79**, 4729 (1957).

(4) J. G. Traynham and O. S. Pascual, *J. Org. Chem.*, **21**, 1362 (1956).

(5) J. G. Traynham and O. S. Pascual, Abstracts of Papers, 131st Meeting of the American Chemical Society, Miami, Fla., April, 1957, p. 45-O.

(6) G. A. Lutz, A. E. Bearse, J. E. Leonard and F. C. Croxtou, *THIS JOURNAL*, **70**, 4139 (1948).

(7) R. B. Turner and R. H. Garner, *ibid.*, **79**, 253 (1957).