t-Butylbenzene was synthesized from *t*-butyl chloride and benzene in the usual way. Its infrared spectrum was checked with Serial No. 414, A.P.I. Project No. 44.

Isoöctane (2,2,4-trimethylpentane) was Merck Reagent, suitable for spectrophotometric use.

Aluminum chloride was B. and A., Anhydrous Sublimed, Reagent.

Infrared analysis was made by means of a Baird Associates model No. 4–55 double-beam recording spectrophotometer, equipped with sodium chloride optics. The absorption peaks which were most useful were: isobutylbenzene, 8.5, 9.0, 9.1, 13.5 μ; *sec*-butylbenzene, 10.0, 10.4, 13.1 μ. Analyses of the products of expts. 1–4 (Table I) were made on pure liquid samples in cells of about 0.02-mm. thickness. The other analyses were made on isoöctane solutions containing 5% by weight of butylbenzenes, using a sample cell of 0.188-mm. thickness and a reference cell (filled with solvent) of 0.187-mm. thickness. The spectra of 5% isoöctane solutions of pure *sec*-butylbenzene, isobutylbenzene and 20–80%, 40–60%, 60–40% and 80–20% mixtures were recorded using the same cells. These spectra were the basis of construction of a plot of optical density at 13.1 and 13.5 μ *vs.* percentage composition of mixtures of the two butylbenzenes. This plot is available on microfilm.[17] The analyses of the butylbenzene fractions from expts. 5–17 were made by comparison of the absorption of their solutions at 13.1 and 13.5 μ with this plot. Complete spectrograms (2–16 μ) of the pure butylbenzene fractions were also made in most of the expts. for qualitative comparisons.

Treatment of *sec*-Butylbenzene and Isobutylbenzene with Aluminum Chloride.—The conditions of temperature, catalyst and time of treatment are given in Table I. In all expts., the hydrocarbon and aluminum chloride were stirred continuously in a round-bottomed flask equipped with a reflux condenser protected by a calcium chloride tube. In most experiments, the amount of butylbenzene treated was 34 g. At the conclusion of the catalyst treatment, cold water was added cautiously and the hydrocarbons were isolated as described previously. The benzene, butylbenzene, and, in some experiments, the dibutylbenzene fractions were separated by distillation through a 50-cm. glass helices-packed column (expts. 1–4) or an 80-cm. Nichrome spiral column (expts. 5–17). The butylbenzene fractions were collected over a boiling range of 165–175° in expts. 1–4, and 170–172.5° in expts. 5–17.

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[17] Deposited as Document number 5709 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting in advance $1.25 for photoprints, or $1.25 for 35 mm. microfilm payable to: Chief, Photoduplication Service. Library of Congress.

AUSTIN 12, TEXAS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE]

The Direction of Elimination in the Pyrolysis of Acetates[1]

BY DONALD H. FROEMSDORF, CAROL H. COLLINS, GEORGE S. HAMMOND AND CHARLES H. DEPUY[2]

RECEIVED MAY 12, 1958

The pyrolysis of a number of aliphatic and alicyclic acetates has been re-examined. The products were analyzed by gas chromatography. The most striking result is the randomness in the reaction. Superimposed upon the nearly statistical results are small electronic and steric effects which often oppose each other. The pyrolysis of 1-alkylcyclohexyl acetates gives predominantly endocyclic olefins. It is suggested that, in contrast to the pyrolysis of amine oxides, the transition state in acetate pyrolysis does not require exact eclipsing of the hydrogen and the acetoxyl group.

The pyrolysis of acetates is a useful procedure for the preparation of many unsaturated compounds. Applied to primary acetates, which can give only a single elimination product, the reaction is often the method of choice for the preparation of pure olefins. Although secondary and tertiary acetates might be expected to give mixtures of products, it has been recently reported[3,4] that such esters show remarkable specificity in pyrolysis. That olefin which would be predicted by the Hoffman rule,[5] *i.e.*, the least substituted ethylene, was believed to be formed nearly exclusively. We have recently reported that the pyrolysis of 1,3-diaryl-2-propyl acetates gives predominantly the more stable olefins[6] (*i.e.*, Saytzeff rule[5]). Consideration of the results led us to re-examine the pyrolysis of aliphatic acetates. The study was facilitated by the use of gas chromatography as an analytical tool. The results obtained are not in agreement with the previously published generalization.[3,4] In one instance we have been able to show that results, based upon infrared analyses previously obtained in this Laboratory, are in error.[7] In fact, with a single possible exception, all pyrolyses gave mixtures.

Results

A series of aliphatic acetates was first studied for comparison with earlier results. The reactions were carried out by dropping pure, liquid esters into the top of a vertical Vycor or Pyrex tube which was packed with Pyrex helices or beads. Pyrolysis tubes were heated externally. A slow stream of nitrogen was used to sweep the gases through the tube and products were collected in a Dry Ice trap. The conversion was determined by titration of the acetic acid in aliquots from the product mixtures. Low-boiling, olefinic products were usually separated from acetic acid and unreacted ester by distillation and the distillate was analyzed by gas chromatography. High boiling reaction mixtures, and occasionally low boiling products, were sampled directly and the samples of unrectified pyrolysate were chromatographed. The product mixture from the pyrolysis of 1-methylcyclohexyl acetate was also analyzed by nuclear magnetic resonance absorption spectroscopy.[8] Examination of the infrared spectrum of the same mixture showed that agreement with the other two analytical

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[1] This research was supported by grants from the Petroleum Research Fund administered by the American Chemical Society and from the Office of Ordnance Research. Grateful acknowledgment is hereby made to the donors of said funds.

[2] To whom inquiries and requests for reprints should be sent.

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

[4] W. J. Bailey, J. J. Hewitt and C. King, *ibid.*, **77**, 357 (1955).

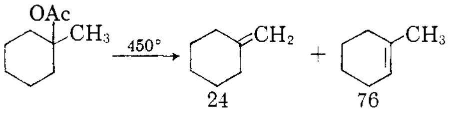
[5] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 427.

[6] C. H. DePuy and R. E. Leary, THIS JOURNAL, **79**, 3705 (1957).

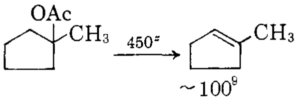
[7] T. D. Nevitt and G. S. Hammond, *ibid.*, **76**, 4124 (1954).

[8] We are indebted to Dr. Keith McCallum, Rohm and Haas Co Redstone Arsenal Research Division, for the nuclear magnetic resonance analysis.

methods could be obtained. The results from the pyrolysis of the aliphatic acetates are summarized in Table I and those obtained with alicyclic acetates are presented in equations 1 through 5.



(1)



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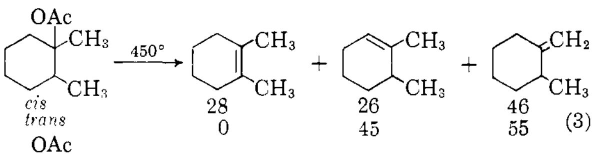

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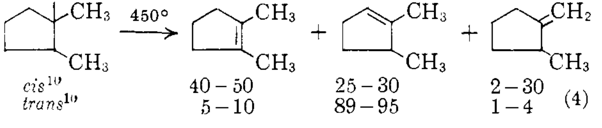

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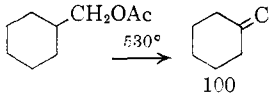

(5)

The wide discrepancy between our results and the previous reports led us to undertake a rather extensive investigation of reaction conditions. Table II summarizes the results of the study with 1-methylcyclohexyl acetate. The only trend observed was an increase in the amount of endocyclic olefin produced in the presence of acid-washed packing. The possibility that the surface of the packing could be conditioned during a run was investigated by pyrolyzing 100 g. of acetate. The product was collected in six fractions. The ratio of the amounts of the olefinic products in different fractions varied by only ±0.3% from the average. The olefin ratios were shown to be relatively insensitive to changes in pyrolysis temperature (*vide infra*). Duplicate pyrolyses carried out by two different workers, using different pyrolysis tubes, gave precisely concordant results.

TABLE I

RELATIVE PERCENTAGES OF OLEFINS FORMED IN ACETATE PYROLYSES[a]

	Acetate	Temp., °C.	1-Olefin	2-Olefin	1-Olefin (calcd.)[b]
(1)	$CH_3CH_2\underset{OAc}{CH}CH_3$	450[c]	57	43[d]	60
(2)	$CH_3CH_2CH_2CH_2OAc$	500	100		
(3)	$(CH_3)_2\underset{OAc}{C}CH_2CH_3$	400[c]	76	24	75
(4)	$(CH_3)_2CH\underset{OAc}{CH}CH_3$	450[c]	80	20	75
(5)	$(CH_3)_2CHCH_2CH_2OAc$	500	100		
(6)	$(CH_3)_2CHCH_2\underset{OAc}{CH}CH_3$	500	53[e]	47[e]	60
			3-Olefin	2-Olefin	3-Olefin (calcd.)[b]
(7)	$(CH_3)_2CH\underset{OAc}{CH}CH_2CH_2CH_3$	450	73	27	67

[a] Averages of 2 to 4 runs. In no case did an individual run vary more than 2% from the average. [b] On a statistical basis; see text. [c] These acetates were pyrolyzed at more than one temperature with little or no effect on olefin ratios; see discussion of results. [d] 28% *trans*, 15% *cis*. [e] Approximate value based on peak height due to incomplete resolution.

Discussion

The data in Table I show that the least highly substituted ethylene predominates among the products of aliphatic acetates. The last column in the table shows the results which would be expected if the choice among β-hydrogens for the elimination were purely statistical. While some of the agreenent with predictions based upon a random process will be shown to be fortuitous. the tendency for elimination to be non-descriminating is clear-cut. Although the two reactions are similar in this respect, acetate pyrolysis is even less selective than the pyrolysis of amine oxides.[11,12] Probably the most significant feature of the results is the implication that competition among various possible elimination paths is very evenly balanced in a number of cases. Such a result would hardly be expected on an *a priori* basis since all of the reactions are probably single-step processes having high activation energies.

Closer examination of the data show that deviations from random elimination can be interpreted in a reasonable way. For example, in the mixture of 2-butenes obtained from 2-butyl acetate the *trans* isomer predominates over the *cis* in a ratio of nearly 2:1. The difference is probably due to a small amount of steric strain, arising from the eclipsing of non-participating methyl groups, in the transition state which leads to the *cis* isomer. A similar "*cis* effect"[13] has previously been observed in the pyrolysis of 1,2-diphenylethyl acetate.[14] The ratio of *trans*-2-butene to 1-butene in the pyrolysate from 2-butyl acetate is approximately 1:2 which is greater than the expected value of 1:3 for a completely random reaction. The deviation from statistical expectation is in the direction of favoring the more highly substituted ethylene although the effect is not large enough to lead to an actual predominance of 2-butene. The result is probably related to the fact that 2-butene is slightly more stable than 1-butene. The difference in stability is due to differences in the heats of formation of the isomers (2 kcal. at 18°)[15] which suggests that the 2-olefin, and the corresponding transition state, are slightly stabilized by small electronic factors such as hyperconjugation.

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(9) See Discussion.

(10) The olefin composition gradually changed on standing, and the amount of exocyclic isomer present diminished. Hence these are probably minimum values for the *exo*-olefin.

(11) A. C. Cope, N. A. LeBel, H. H. Lee and W. R. Moore, THIS JOURNAL, **79**, 4720 (1957).

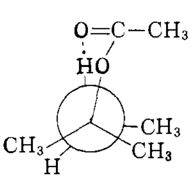
(12) A. C. Cope, C. L. Bumgardner and E. E. Schweizer, *ibid.*, **79**, 4729 (1957).

(13) D. Y. Curtin, *Rec. Chem. Progr.*, **15**, 111 (1954).

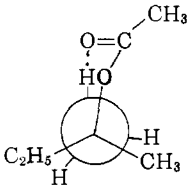
(14) D. Y. Curtin and D. B. Kellom, THIS JOURNAL, **75**, 6011 (1953).

(15) Bichowsky and Rossini, "Thermodynamics of Chemical Substances," Reinhold Publishing Corp., New York, N. Y., 1936.

Similar arguments can be applied to other examples shown in Table I. The very close agreement between the actual product distribution from *t*-amyl acetate and that calculated for the random process may be due in part to cancelation of electronic factors, which would favor the formation of trimethylethylene, and transition-state eclipsing effects, which would favor the production of the terminal olefin. Presumed configurations of the two transitions states are



Transition state for formation of $(CH_3)_2C{=}CHCH_3$



Transition state for formation of $C_2H_5C(CH_3){=}CH_2$

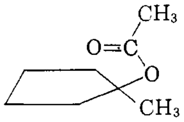
On the whole, the pyrolysis of alicyclic acetates shows trends reminiscent of those reported for the corresponding amine oxides.[12] The principal difference between the reactions is the lower specificity of acetate pyrolysis. Since the cyclic transition state in acetate decomposition involves a six-membered ring and that for the amine oxide reaction is five-membered, it is not surprising that the former imposes less rigorous steric requirements. Comparison between the two reactions and examination of the individual results indicate that perfect eclipsing of hydrogen and the acetoxyl group is not required for acetate pyrolysis.

Results summarized in equations 1-5 show that: (1) methylcyclohexyl acetate gives 1-methylcyclohexene and methylenecyclohexane in the ratio 3:1, (2) methylcyclopentyl acetate either gives exclusively endocyclic olefin or a mixture of olefins which cannot be resolved by gas chromatography with the columns which we have used and (3) pyrolysis of the *cis* and *trans* isomers of 1,2-dimethylcyclohexyl acetate and 1,2-dimethylcyclopentyl acetate shows the gross stereospecificity which has been associated with ester pyrolysis.[16]

Methylcyclohexyl acetate was studied exhaustively since four previous reports indicated that the ester is pyrolyzed to give methylenecyclohexane as a principal product.[4,7,17,18] Furthermore, N,N-dimethyl-1-methylcyclohexylamine oxide gives the exocyclic olefin almost exclusively.[12] Accumulated evidence includes agreement between G.P.C. and n.m.r. analyses and wide variations in reaction conditions. The evidence is overwhelming in favor of the view that the product composition reported in this paper is correct and reproducible. The results are easily understood if the transition state for acetate pyrolysis can be formed without appreciable strain from an equatorial acetoxyl group and an adjacent axial hydrogen. The statistical preference for formation of the exocyclic olefin is compensated by the fact that a free rotation of the methyl group must be lost in the elimination, whereas *cis*-elimination involving a ring hydrogen can occur with a minimum restriction of internal motion of the molecule.[19] In addition, the well recognized stability of endocyclic olefins with respect to their exocyclic isomers[20] should favor the formation of 1-methylcyclohexene.

The olefinic product from 1-methylcyclopentyl acetate was eluted from all chromatographic columns which were tried as a single fraction having the same retention time as authentic 1-methylcyclopentene. Since authentic methylenecyclopentane has not been prepared, we cannot be certain that the product is not an unresolved mixture. Examination of the infrared spectrum of the product shows no appreciable absorption near the 890 cm.$^{-1}$ region. We infer that methylenecyclopentane was either absent or present in small amount.[21]

If 1-methylcyclopentyl acetate gives either predominantly or exclusively 1-methylcyclopentene on pyrolysis, the result may be attributed to the fact that the acetoxyl group of the ester is held close to two adjacent ring hydrogens. Examination of models indicates that in the stable configuration of the ester the acetoxyl group lies over the cyclopentane ring, as



Addition of an adjacent *cis*-methyl group to 1-methylcyclopentyl acetate results in an increase in the amount of exocyclic olefin formed in pyrolysis. Models show that free rotation of the methyl groups is no longer possible and as a consequence the transition state for formation of *exo*-olefin does not involve loss of free rotation and is, therefore, relatively more favorable than is the case in the monomethyl compound.

Table II summarizes some of our experiments designed to determine whether conditions could be found under which higher percentages of *exo*-olefin are formed, as had been reported in earlier work. Only under acidic conditions did the olefin composition differ from that found normally, and in those cases a higher percentage of *endo*-olefin (*i.e.*, Saytzeff product) was produced. In fact in the course of over one hundred pyrolyses we have always observed consistent and reproducible results, except in those cases (*e.g.*, with H_2SO_4) in which acidic reagents were used.

In several experiments we pyrolyzed primary acetates and in every case only a single olefin was

[16] E. R. Alexander and A. Mudrak, This Journal, **72**, 1810 (1950).

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

[18] S. Siegel and M. Dunkel, Abstracts of 129th National Meeting, Dallas, Texas, April 8–13, 1956, p. 28N.

[19] Dr. J. C. Martin (University of Illinois) has pointed out the fact that, because of the difference between freely rotating and rigidly oriented groups, the statistical availability of hydrogen in mixed alkyl-alicyclic systems is not obtained by simple counting procedures. Thus at any given time, only two hydrogens of the methyl group can be as available as the two *cis* ring hydrogens. Therefore on a statistical basis alone, the *exo–endo* ratio should be close to one.

[20] R. B. Turner and R. H. Garner, This Journal, **79**, 253 (1957); **80**, 1424 (1958).

[21] See the accompanying paper by W. J. Bailey and W. F. Hale, *ibid.*, **81**, 647 (1959). These authors report that they obtained 15% methylenecyclopentane in the pyrolysis of 1-methylcyclopentyl acetate. We are indebted to Prof. Bailey for the communication of this, and other results, in prepublication correspondence.

TABLE II

EFFECT OF REACTION CONDITIONS ON THE PRODUCT COMPOSITION IN THE PYROLYSIS OF 1-METHYLCYCLOHEXYL ACETATE

Packing	Temp., °C.	Endo, %	Remarks
Desicote on helices	350	76	
NaOH on helices	450	82	Charring
Acid-treated silica	350	99	
H_2SO_4 on helices	450	99	Charring
Helices	350	72	
Helices	450	74	
Helices	550	74	

produced, indicating that no equilibration was taking place during the course of pyrolysis. We also pyrolyzed *n*-butyl acetate in the presence of pure *cis*-2-butene. The product of this pyrolysis was a mixture of 1-butene and *cis*-2-butene containing no *trans*-2-butene, showing that there was no *cis–trans* interconversion under the conditions. In several cases the crude pyrolysate was passed again through the pyrolysis tube. The olefin composition was not changed by recycling.

The olefinic products from pyrolysis of the 1,2-dimethylcyclopentyl acetates were unstable and the olefin ratios were dependent upon the method of treatment of the pyrolysate. If the reaction mixture was allowed to stand, the ratios of olefinic products changed. The change was most rapid in samples which had come in contact with air. This behavior appears to be a property of the olefins and is not unique to the pyrolysis products, for olefinic mixtures produced in other ways also change composition upon standing.[22]

In an attempt to determine the effect of temperature upon the ratio of olefins being formed, we carried out several pyrolyses at more than one temperature. The results in Table II for 1-methylcyclohexyl acetate indicate that the product is not sensitive to temperature. We have found this to be true for a number of other olefins, as indicated in Table I. In particular we pyrolyzed *t*-amyl acetate at 350, 400 and 500° without changing the olefin ratios more than 3%. Since no accurate trend was obtained we consider that the ratio of products formed are not sensitive to temperature.

Experimental

2-Butanol, *t*-amyl alcohol, 4-methyl-2-pentanol, 3-methyl-1-butanol, cyclohexylmethanol and ***n*-butyl acetate** were commercial materials which were fractionated by distillation through efficient columns before use.

3-Methyl-2-butanol was prepared by the reduction of isopropyl methyl ketone with lithium aluminum hydride, b.p. 110–111° (740 mm.) (lit.[23] b.p. 111–112°).

2-Methyl-3-hexanol was prepared from *n*-butyraldehyde and isopropylmagnesium bromide, b.p. 144–145° (742 mm.) (lit.[24] b.p. 144–145°).

1-Methylcyclohexanol was prepared by the addition of cyclohexanone to methylmagnesium iodide, b.p. 53.0–53.5° (9 mm.) (lit.[7] b.p. 68° (24 mm.)).

1-Methylcyclopentanol was prepared by the addition of cyclopentanone to methylmagnesium chloride, b.p. 45–46° (15 mm.) (lit.[25] b.p. 82 (100 mm.)).

1,2-Dimethylcyclohexanols were prepared and separated by distillation essentially by procedures previously described.[7]

1,2-Dimethylcyclopentanols.—The starting material, 2-methylcyclopentanone, was prepared by the sequence cyclization of diethyl adipate to ethyl cyclopentanone-2-carboxylate with sodium hydride (75% yield), reaction of the ketoester with sodium hydride, followed by alkylation with methyl iodide to give ethyl 2-methylcyclopentanone-2-carboxylate (81% yield) and hydrolysis and decarboxylation of the last product by refluxing with 2 *N* hydrochloric acid (65% yield). A mixture of *cis*- and *trans*-1,2-dimethylcyclopentanol was prepared by the addition of 2-methylcyclopentanone to freshly prepared methylmagnesium chloride (50% yield). The alcohols were separated by distillation through a 50-plate, concentric tube column. The *cis*:*trans* ratio was 7:3; *cis*-alcohol, b.p. 59.5–61.0° (17 mm.), lit.[26] 69.6 (25 mm.); *trans*-alcohol b.p. 50.0–51.2° (16 mm.), lit.[26] 58.4° (24 mm.).

2-Butyl acetate, 3-methyl-2-butyl acetate, 3-methyl-1-butyl acetate, 4-methyl-2-pentyl acetate, 2-methyl-3-hexyl acetate and cyclohexylmethyl acetate were prepared by acylation of the corresponding alcohols with acetic anhydride and pyridine. Their physical properties were in agreement with literature values.

***t*-Amyl acetate and the cyclic acetates** were prepared by acetylation with dimethylaniline and acetyl chloride.[7] Their boiling points are listed in Table III.

TABLE III

BOILING POINTS OF ACETATES

Acetate	B.p. °C.	B.p. Mm.	Lit. b.p. °C.	Lit. b.p. Mm.	Ref.
t-Amyl	121–121.5	740	124–125		27
1-Methylcyclohexyl	67.5–68	14	74	20	7
1-Methylcyclopentyl	55.5–57	19	155–156		17
cis-1,2-Dimethyl-cyclohexyl	80–82	22	84	18	7
trans-1,2-Dimethyl-cyclohexyl	77–78	21	78	20	7
cis-1,2-Dimethyl-cyclopentyl	70.5–71	19			
trans-1,2-Dimethyl-cyclopentyl	65.5–66	19			

Butenes.—1-Butene was prepared by pyrolysis of *n*-butyl acetate and by reaction of 1-bromobutane with potassium *t*-butoxide. A mixture of 1-butene, *cis*-2-butene and *trans*-2-butene was prepared by treatment of 2-bromobutane with potassium ethoxide. These were identified by comparison with the expected amounts of olefins in E_2 eliminations.[28]

Pentenes.—3-Methyl-1-butene was prepared by pyrolysis of 3-methyl-1-butyl acetate and by elimination from 3-methyl-1-bromobutane with base. 2-Methyl-1-butene was formed by pyrolysis of 2-methyl-1-butyl acetate. 2-Methyl-2-butene was prepared by dehydration of 3-methyl-2-butanol in the presence of sulfuric acid.

Hexenes.—3-Methyl-1-pentene and 3-methyl-2-pentene were prepared by dehydration of 3-methyl-2-pentanol. The major product was assigned the more highly substituted structure.[29]

Heptenes.—The assignment of structure to the products of the pyrolysis of 2-methyl-3-hexyl acetate was made on the basis of retention volumes, with the assumption that the lower retention volume corresponded to the olefin of lower boiling point. It has been reported[30] that 2-methyl-3-hexene boils at 85–86° and 2-methyl-2-hexene at 94.4–94.6° (760 mm.).

1-Methylcyclohexene was prepared by iodine-catalyzed dehydration of 1-methylcyclohexanol.[31] The infrared spectrum supported its structure and gas chromatography

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(22) C. H. Collins, unpublished results.

(23) F. L. Gustus and P. G. Stevens, THIS JOURNAL, **55**, 385 (1933).

(24) F. C. Whitmore and F. Johnston, *ibid.*, **60**, 2265 (1938).

(25) N. Zelinsky and S. Namjetkin, *Ber.*, **35**, 2683 (1902).

(26) G. Chiurdoglu, *Bull. soc. chim. Belg.*, **44**, 527 (1935).

(27) J. C. Munch, THIS JOURNAL, **48**, 997 (1926).

(28) (a) H. C. Brown and O. H. Wheeler, *ibid.*, **78**, 2200 (1956); (b) G. P. C. analysis showed 20% 1-butene, 21% *cis*-2-butene, 59% *trans*-2-butene; (c) our retention volumes of the butenes agreed well with those found on a similar column by A. I. M. Keulemans, A. Kwantes and P. Zaal, *Anal. Chim. Acta*, **13**, 365 (1955).

(29) A. L. Henne and A. H. Matuszak, THIS JOURNAL, **66**, 1649 (1944).

(30) F. V. Sodaz and C. E. Boord, *ibid.*, **55**, 3293 (1933).

(31) W. A. Mosley, *ibid.*, **62**, 562 (1940).

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 μ region (no $=CH_2$), b.p. 74.8° (730 mm.), lit.[32] 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.[33] 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.[7] 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.

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 × 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.[35]

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.

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(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).

(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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Pyrolysis of Esters. XV. Effect of Temperature on Direction of Elimination of Tertiary Esters[1]

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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[3] had shown that the pyrolyses of amides were not as selective as had been reported originally for esters.[4] 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

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(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).