[Contribution from the Department of Chemistry, University of Maryland]

Pyrolysis of Esters. IX. Pyrolysis of 2-Methylcyclohexyl Acetate[1]

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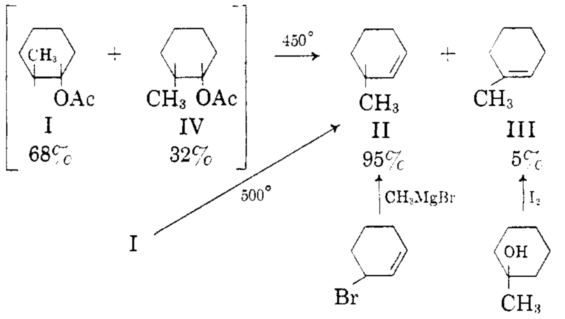
In contrast to the work of Arnold, Smith, and Dodson, the pyrolysis of a mixture of *cis*- and *trans*-2-methylcyclohexyl acetates or pure *trans*-2-methylcyclohexyl acetate produced almost entirely 3-methylcyclohexene with only a trace of the isomeric 1-methylcyclohexene. These results are in agreement with earlier work which showed that in the pyrolysis of open-chain esters the least highly alkylated olefin was formed in a very high yield. It was found that very high temperatures promoted extensive charring and gasification and caused rearrangements and aromatization. The presence of a carbonaceous deposit was found to reverse to some extent the direction of elimination during the pyrolysis of esters.

It was recently reported[3,4] that the pyrolysis of simple esters proceeded in a selective manner to produce the least highly alkylated olefin according to the Hofmann rule. The hydrogen that was abstracted during the pyrolysis was abstracted preferentially from a $CH_3 > CH_2 > CH$. Thus the pyrolysis of methylisopropylcarbinyl acetate gave almost pure 3-methyl-1-butene and of methylisobutylcarbinyl acetate gave 4-methyl-1-pentene. The presence of polar groups, such as methoxy and dimethylamino groups in the β-position, does not change the direction of elimination.[5] A phenyl group will partially reverse the direction of elimination while an unsaturated electron-withdrawing group located in the β-position will completely reverse the direction of elimination to produce the conjugated olefin.[6]

There are, however, many examples in the literature in which an ester was pyrolyzed to give a mixture of olefins or the most highly alkylated olefin in direct conflict with these results. Thus Arnold, Smith, and Dodson[7] found that the pyrolysis of *cis*-2-methylcyclohexyl acetate (IV) produced a mixture consisting of 75% of 3-methylcyclohexene (II) and 25% of 1-methylcyclohexene (III), while the pyrolysis of *trans*-2-methylcyclohexyl acetate (I) produced a mixture consisting of 45% of II and 55% of III. Our work with the open-chain esters would lead to the prediction that both the *cis*- and *trans*-2-methylcyclohexyl acetates (I and IV) would give primarily the least highly alkylated olefin II.



Wibaut and van Pelt[8] originally reported that the pyrolysis of *l*-menthyl acetate gave an 88% yield of 3-*p*-menthene. This result was confirmed by Frank and Berry.[9] Later, Wibaut, Beyerman, and van Leeuwen[10] and also McNiven and Read[11] reinvestigated this pyrolysis and reported that *l*-menthyl acetate produced a mixture of olefins consisting of 65% 3-*p*-methene and 35% 2-*p*-methene. Warnhoff and Johnson[12] obtained 2-methyl-2-cyclohexenone from the pyrolysis of 2-methyl-2-acetoxycyclohexanone. Chitwood[13] was able to obtain crotyl acetate and methylvinylcarbinyl acetate but no 3-butenyl acetate from the pyrolysis of 1,3-diacetoxybutane. There are many examples in the field of steroids[14-17] that also conflict with our results.[3,4] Barton and Rosenfelder[14] even assigned structures to their starting esters on the basis of the structures of the olefins that they obtained from the pyrolysis of two geometric isomers.

The work of Alexander and Mudrak[18] on the pyrolysis of *cis*- and *trans*-2-phenylcyclohexyl acetates may not be in conflict with our work since we have shown that the introduction of a β-phenyl group into the alkyl portion of an ester partially

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(1) Previous paper in this series, *J. Org. Chem.*, **21**, 648 (1956).

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(3) Bailey and King, *J. Am. Chem. Soc.*, **77**, 75 (1955).

(4) Bailey, Hewitt, and King, *J. Am. Chem. Soc.*, **77**, 357 (1955).

(5) Bailey and Nicholas, *J. Org. Chem.*, **21**, 648 (1956).

(6) Bailey and King, *J. Org. Chem.*, **21**, 858 (1956).

(7) Arnold, Smith, and Dodson, *J. Org. Chem.*, **15**, 1256 (1950).

(8) Wibaut and van Pelt, *Rec. trav. chim.*, **60**, 55 (1941).

(9) Frank and Berry, *J. Am. Chem. Soc.*, **72**, 2988 (1950).

(10) Wibaut, Beyerman, and van Leeuwen, *Rec. trav. chim.*, **71**, 1027 (1952).

(11) McNiven and Read, *J. Chem. Soc.*, 2067 (1952).

(12) Warnhoff and Johnson, *J. Am. Chem. Soc.*, **75**, 494 (1953).

(13) Chitwood, U. S. Patent 2,251,983 (1941).

(14) Barton and Rosenfelder, *J. Chem. Soc.*, 1048 (1951).

(15) Plattner, Heusser, Troxler, and Segré, *Helv. Chim. Acta*, **31**, 852 (1948).

(16) Haslewood, *Biochem. J.*, **33**, 454 (1939).

(17) Barton and Rosenfelder, *J. Chem. Soc.*, 2459 (1949).

(18) Alexander and Mudrak, *J. Am. Chem. Soc.*, **72**, 3194 (1950).

reverses the direction of elimination to produce a mixture of the two possible olefins.[6]

Since most of the examples in which the pyrolysis gave an olefin that would not have been predicted from our own work[3,4] pertained to cyclic esters, it was of interest to determine the effect of the cyclohexane ring on the direction of elimination. For this reason the work of Arnold, Smith, and Dodson on the pyrolysis of *cis*- and *trans*-2-methylcyclohexyl acetates (I and IV) was reinvestigated.

Since the separation of the pure isomers I and IV was very tedious, the initial studies were carried on with a mixture of these two geometric isomers. A mixture of *cis*- and *trans*-2-methylcyclohexanols was prepared by the catalytic hydrogenation of *o*-cresol and was assumed to contain 68% of the *trans*-isomer, in accord with Jackman, Macbeth, and Mills [19] If the mixture of acetates I and IV contained 68% of the *trans*-isomer I, Arnold's work would lead one to predict that the mixture of the olefins obtained on pyrolysis would contain 55% of 3-methylcyclohexene (II) and 45% of 1-methylcyclohexene (III). If the pyrolysis followed the pattern found in the open-chain esters, one would predict that the product would be almost entirely the 3-methyl isomer II.

This mixture of the *cis*- and *trans*-esters I and IV was dropped through a vertical Vycor tube packed with $^1/_8$-inch Pyrex helices at 450° under such conditions that only 52% of the theoretical amount of acetic acid was liberated. Under these conditions, practically no charring occurred that could cause any rearrangement or aromatization.[20] The olefin obtained from the pyrolysis was at least 95% 3-methylcyclohexene (II). II was identified by the comparison of its physical properties with those of an authentic sample prepared by an independent synthesis. The infrared absorption spectra of the two samples of II were practically identical. The sample of 3-methylcyclohexene (II) used for comparison was prepared from cyclohexene by bromination with N-bromosuccinimide and by the reaction of the resulting allylic bromide with methylmagnesium bromide.[21] A sample of 1-methylcyclohexene (III) was prepared by the dehydration of cyclohexanol. The infrared absorption spectrum of III was sufficiently different from that of II to make the detection of III quite sensitive.

It appears, therefore, that the direction of elimination in the pyrolysis of cyclic esters is governed by the same rules that apply to the open-chain esters. Thus the hydrogen will be preferentially abstracted from the CH_2 group rather than from a CH group in the cyclohexane system as well as in open-chain esters. The relative steric relationship of the tertiary hydrogen and the acetoxy group does not appreciably affect this preference.

TABLE I

PYROLYSIS OF THE MIXTURE OF *cis*- AND *trans*-2-METHYLCYCLOHEXYL ACETATES

Run No.	Pyrolysis Temp., °C.	Acetic Acid Liberated, %	Yield of Olefin, %	n_D^{25}	Minimum Amount of 3-Methylcyclohexene, %
1	450	52	93	1.4419–1.4437	95
2	500	97	96	1.4418–1.4454	93
3	500	98	98	1.4418–1.4428	98
4[a]	560	100	93	1.4420–1.4454	91[b]
5[c]	600	100	88	1.4420–1.4476	62[d]
6[e]	500	98	95	1.4419–1.4472	85

[a] Some charring occurred. [b] Small amount of material other than II and III present. [c] Extensive charring and gasification occurred. [d] Large amount of material other than II and III present. [e] Pyrolysis tube previously coated with a carbonaceous deposit.

An effort was made to determine the reason for the conflict between the present results and those obtained by Arnold, Smith, and Dodson.[7] Of course, they carried out their pyrolysis in a stainless steel tube while our pyrolysis was carried out over Pyrex helices. There has been a great deal of information published that would indicate that, as long as the surface is inert, it does not make much difference whether the packing of the pyrolysis tube is Pyrex, quartz, carborundum, stainless steel, or aluminum.[22,23]

Unless the particular type of stainless steel tube that was used had some unusual catalytic activity, it does not appear likely that the change in packing and tube could account for the significant difference in the products.

Since Arnold, Smith, and Dodson carried out their study at 500°, it appeared that these more vigorous conditions might be responsible for the formation of the 1-methylcyclohexene (III) from the 2-methylhexyl acetates I and IV. For this reason the mixture of *cis*- and *trans*-acetates I and IV was pyrolyzed at 500° under a variety of addition rates and contact times. In all cases, only slight carbonization occurred even though as much as 98% of the theoretical amount of acetic acid was liberated. The olefin obtained in every case consisted of 93 to 98% 3-methylcyclohexene (II). 1-Methylcyclohexene (III) was identified as another component which was present as up to 7% of the product. Since the effect of temperature at 500° was slight, a pyrolysis was carried out at 560°. A substantially quantitative yield of acetic

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(19) Jackman, Macbeth, and Mills, *J. Chem. Soc.*, 1717 (1949).

(20) Bailey and Rosenberg, *J. Am. Chem. Soc.*, **77**, 73 (1955).

(21) Wilkinson, *J. Chem. Soc.*, 3057 (1931).

(22) Burns, Jones, and Ritchie, *J. Chem. Soc.*, **400**, 714 (1935).

(23) Smith, Fisher, Ratchford, and Fein, *Ind. Eng. Chem.*, **34**, 473 (1942).

acid was realized but heavy carbonization occurred. Even at this relatively high temperature, a 93% yield of a mixture of olefins consisting of 91% of the 3-methyl isomer II was obtained. However, the infrared absorption spectrum indicated the presence of substances other than II and III. At 600° extensive carbonization and gas formation occurred during the pyrolysis. The hydrocarbon fraction was obtained in only 88% yield and it contained only approximately 62% of 3-methylcyclohexene (II). The infrared absorption spectrum indicated that only a small amount of the other hydrocarbons was 1-methylcyclohexene (III). Apparently extensive disproportionation to form cyclohexane or aromatic derivatives and rearrangement to other olefins had occurred. A free radical decomposition of the ester at this elevated temperature was at least partially responsible for these extraneous products. It was clear from these pyrolyses that the difference in temperatures of pyrolysis alone could not explain the formation of the large amount of 1-methylcyclohexene obtained by Arnold, Smith, and Dodson.

It appeared more likely that a carbonaceous deposit formed during the pyrolysis was responsible for the formation of the 1-methyl isomer (III). Since a stainless steel tube cannot be cleaned as conveniently as a glass tube and the extent of carbonization is much more difficult to determine in a metal tube, it seemed likely that a layer of carbonaceous material could have been present in their pyrolysis tube. For this reason a pyrolysis was carried out at 500° in a tube containing a carbonaceous deposit. When the mixture of *cis-* and *trans*-2-methylcyclohexyl acetates (I and IV) was pyrolyzed under these conditions, a mixture of olefins which contained at least 15% of the 1-methylcyclohexene was obtained. It seems possible that a heavier or more acidic deposit could have been responsible for the large amount of the 1-methyl isomer obtained by Arnold, Smith, and Dodson. At least it has been demonstrated that the presence of carbon deposits will promote a direction of elimination in the pyrolysis of an ester that is different from that obtained in the absence of carbon. It had been shown previously[24] that carbon deposits increased the extent of pyrolysis. Although the acidic carbon deposit may have rearranged some of the 3-methyl compound to the more stable 1-methyl isomer during the pyrolysis, it appears more probable that the carbon promoted a competing acid-catalyzed elimination reaction to produce the 1-methyl isomer directly from the ester.

In order to eliminate the possibility that the difference in the results between our work and that of Arnold, Smith, and Dodson[7] was due to the difference in the starting material, a sample of pure *trans*-2-methylcyclohexyl acetate (I) was prepared according to their directions. When this pure isomer I was pyrolyzed at 500° under conditions such that very little charring occurred, the olefin produced was at least 91% 3-methylcyclohexene (II). Even though some 1-methylcyclohexene (III) was formed under these fairly vigorous conditions, the amount was in striking contrast to the 55% obtained by Arnold, Smith, and Dodson.[7] Of course, even though our results differ in the quantitative nature of the experimental work from that of Arnold, Smith, and Dodson, their conclusions concerning the mechanism of the pyrolysis are not changed.

Several of the other conflicts with our work on the direction of elimination in the pyrolysis of esters are under investigation and these results will be reported separately.

EXPERIMENTAL[25]

Mixture of cis- and trans-2-methylcyclohexanols. According to the procedure of Jackman, Macbeth, and Mills,[20] 800 g. (7.4 moles) of *o*-cresol (Eastman Kodak) was hydrogenated at 150° and 2600 pounds pressure in the presence of Raney nickel catalyst. After the catalyst was removed by filtration, the filtrate was fractionated through a 12-inch, helix-packed column to yield 808 g. (96%) of a mixture of *cis-* and *trans*-2-methylcyclohexanols, b.p. 53–54° (3.5 mm.), n_D^{25} 1.4604. Reported[7] constants for *cis*-2-methylcyclohexanol are b.p. 43–45° (1–2 mm.), n_D^{25} 1.4620, and for *trans*-2-methylcyclohexanol, b.p. 60.7–61° (10.5 mm.), n_D^{25} 1.4596. It was assumed from these constants as well as the method of preparation[20] that the mixture contained 68% *trans*-2-methylcyclohexanol.

Mixture of cis- and trans-2-methylcyclohexyl acetates (I and IV). To 1430 g. (14 moles) of acetic anhydride heated under reflux was added dropwise at such a rate as to maintain the reflux 808 g. (7.1 moles) of the mixture of *cis-* and *trans*-2-methylcyclohexanols. After the reaction mixture had been heated under reflux for 12 hours, the cooled solution was poured into a cold saturated sodium bicarbonate solution. The aqueous layer was extracted with two 500-ml. portions of ether. The extracts were combined with the original organic layer and the mixture was dried over magnesium sulfate. The dried solution was fractionated through a 12-inch, helix-packed column to yield 962 g. (88%) of a mixture of *cis-* and *trans*-2-methylcyclohexyl acetates (I and IV), b.p. 52° (3.5 mm.), n_D^{25} 1.4363 [reported[7] for the *cis*-isomer, b.p. 68.5–69.5° (16 mm.), n_D^{25} 1.4376, and for the *trans*-isomer, b.p. 63–64° (11.5 mm.), n_D^{25} 1.4353].

trans-2-Methyclyclohexyl 3,5-dinitrobenzoate. A mixture of 460 g. (2.0 moles) of 3,5-dinitrobenzoyl chloride, 1500 g. of pyridine, and 228 g. (2.0 moles) of a mixture of *cis-* and *trans*-2-methylcyclohexanols was heated at 60° for 2 hours and then the cooled mixture was poured into a large excess of water. Seven recrystallizations of the precipitate from methanol produced 292 g. (36%) of *trans*-2-methylcyclohexyl 3,5-dinitrobenzoate, m.p. 114.5–116° (reported[7] m.p. 113.5–115°).

trans-2-Methylcyclohexanol. A mixture of 292 g. (0.95 mole) of *trans*-2-methylcyclohexyl 3,5-dinitrobenzoate, 302 g. (5.4 moles) of potassium hydroxide, 2400 ml. of methyl alcohol, and 1100 g. of water was heated under reflux for 2

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[24] Bailey and Hewitt, *J. Org. Chem.*, 21, 543 (1956).

(25) The authors are grateful to Dr. Robert A. Spurr, Dr. Joseph Wenograd, and Kathryn Gerdeman for the infrared absorption spectra. The spectra were obtained on the pure liquids by the use of a Perkin-Elmer model 12-C infrared spectrophotometer, modified for double-pass operation.

hours. The reaction mixture was exhaustively extracted with ether and the extracts were fractionated through a 6-inch, helix-packed column to yield 93 g. (87%) of *trans*-2-methylcyclohexanol, b. p. 52° (5 mm.), n_D^{25} 1.4597 [reported[7] b.p. 60.7–61° (10.5 mm.), n_D^{25} 1.4596].

trans-2-Methylcyclohexyl acetate (I). By the use of the same procedure described for the mixture of acetates I and IV, 93 g. of *trans*-2-methylcyclohexanol was esterified to yield 119 g. (94%) of *trans*-2-methylcyclohexyl acetate (I), b.p. 54° (5 mm.), n_D^{25} 1.4353 [reported[7] b.p. 63–64° (11.5 mm.), n_D^{25} 1.4353].

1-Methylcyclohexene (III). To the ether solution of methylmagnesium iodide [prepared from 158 g. (1.1 moles) of methyl iodide] was added dropwise 98 g. (1 mole) of cyclohexanone. The complex was decomposed by the addition of 10% hydrochloric acid, and the resulting ether layer was washed with a sodium bicarbonate solution and then with water. The ether was removed by distillation and the residue, to which had been added 0.5 g. of iodine, was distilled through an 18-inch, helix-packed column. The olefin layer of the distillate was dried over magnesium sulfate and fractionated through the same column to yield 76 g. (79%) of 1-methylcyclohexene (III), b.p. 109–109.5°, n_D^{20} 1.4503 (reported[26] b.p. 109–109.5°, n_D^{20} 1.4503).

3-Methylcyclohexene (II). According to the method of Guillemonat[27] and Wilkinson[21] a mixture of 267 g. (1.36 moles) of N-bromosuccinimide, 120 g. (1.48 moles) of cyclohexene, 1000 ml. of carbon tetrachloride, and 0.5 g. of benzoyl peroxide was heated under reflux for 1 hour. The succinimide was removed by filtration and the filtrate was fractionated through a 6-inch, helix-packed column to yield 149 g. (68%) of 3-bromohexene, b.p. 63–64° (15 mm.), n_D^{25} 1.5261 [reported[27] b.p. 65° (19 mm.), $n_D^{19.5}$ 1.5253].

This 3-bromohexene was added dropwise to an ether solution of methylmagnesium bromide [prepared from 92 g. (0.95 mole) of methyl bromide]. After the mixture had been allowed to stand overnight, the precipitate was removed by filtration and the filtrate was distilled through an 18-inch, helix-packed column to yield 48.5 g. (56%) of 3-methylcyclohexene (II), b.p. 100–101°, n_D^{25} 1.4424 [reported[7] b.p. 100–100.8°, n_D^{20} 1.4442].

Pyrolysis of the mixture of 2-methylcyclohexyl acetates (I and IV). A series of pyrolyses of the mixture of 68% *trans*-2-methylcyclohexyl acetate (I) and 32% *cis*-2-methylcyclohexyl acetate (IV) were conducted under various conditions of temperature, drop rate, and packing of the pyrolysis tube. The results of several representative runs are listed in Table I. A typical pyrolysis is described below for one run at 500°.

In every pyrolysis but one the pyrolysis tube had been carefully cleaned with refluxing nitric acid, followed by extensive washes with water and acetone. In pyrolysis No. 6, a tube that had been purposely coated with a carbon deposit by the pyrolysis of an ester in the presence of a trace of oxygen was used as such without any further treatment.

At the rate of 1.2 g. per minute, 63.8 g. (0.41 mole) of a mixture of *cis*- and *trans*-2-methylcyclohexyl acetates (I and IV) was added dropwise to the top of a Vycor pyrolysis tube packed with $^1/_8$-inch Pyrex helices and externally heated at 500° as described previously.[28] The apparatus was continuously flushed with a slow stream of oxygen-free nitrogen to minimize charring. Very little carbon formation was noted. The pyrolysate was condensed in a 6-inch spiral condenser and collected in a side-inlet flask cooled in a Dry Ice-chloroform-carbon tetrachloride bath. The pyrolysate was extracted with water to remove the acetic acid and the organic layer was dried over magnesium sulfate and potassium carbonate. (Titration of an aliquot of the aqueous extracts indicated that 97% of the theoretical amount of acetic acid had been liberated.) The water-white organic layer was fractionated through an 18-inch, helix-packed column to yield in 16 fractions 37.5 g. (96%) of impure 3-methylcyclohexene (II), b.p. 101–103.5°, n_D^{25} 1.4418–1.4454. For 74% of the olefin fraction n_D^{25} was 1.4418–1.4425 and for the total product n_D^{25} was 1.4423. The purity of the 3-methylcyclohexene (I) was estimated from the refractive indices of each of the fractions and from the infrared absorption spectra of the individual fractions and of the total product. The absorbancies at several peaks in the infrared spectra of both II and III were plotted against concentration from a series of standard mixtures. The middle fractions of the distillation possessed an infrared absorption spectra indistinguishable from the pure 3-methylcyclohexene (II). Only the higher boiling fractions showed any of the isomeric 1-methylcyclohexene (III). The results of these determinations showed that olefin obtained from the pyrolysis contained at least 93% 3-methylcyclohexene (II) and not over 7% 1-methylcyclohexene (III).

Pyrolysis of trans-2-methylcyclohexyl acetate (I). At the rate of 1 g. per minute, 100 g. (0.64 mole) of *trans*-2-methylcyclohexyl acetate (I) was dropped through the apparatus described above which was heated at 500°. The pyrolysate was washed with water to remove the acetic acid and the organic layer was dried over magnesium sulfate and potassium carbonate. (Titration of the aqueous extracts with standard base indicated that 98.5% of the theoretical amount of acetic acid had been liberated.) Fractionation of the organic layer through an 18-inch, helix-packed column yielded 59.2 g. (96%) of slightly impure 3-methylcyclohexene (II), b.p. 101–103°, n_D^{25} 1.4422–1.4440, collected in 18 fractions. Infrared absorption studies on this material indicated that the product was at least 91% 3-methylcyclohexene (II) and not over 9% 1-methylcyclohexene (III).

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(26) Bartlett and Rosenwald, *J. Am. Chem. Soc.*, **56**, 1993 (1934).

(27) Guillemonat, *Ann. chim.*, [11] **11**, 187 (1939).

(28) Bailey and Golden, *J. Am. Chem. Soc.*, **75**, 4780 (1953).