mixture was placed around trap C and the system was evacuated. The catalyst was warmed cautiously with a free flame, evaporating residual ethanol. As heating was continued (to *ca.* 200° as determined by separate experiments employing a heating bath) gases desorbed abruptly from the catalyst, a process accompanied by evolution of heat and light, and samples of these gases were collected in the usual manner for mass spectrographic and radioactivity assays. The data in nos. 5 and 6 of Table I were obtained on gas samples collected in this manner. Radioactivity assay of the gas sample in question followed by appropriate pressure and volume corrections indicated that the sample contained only about 36% of the radioactivity known (no. 5, Table II) to be associated with the residual catalyst. Accordingly, the catalyst remaining after the above vacuum baking was analyzed for additional radioactivity by the usual wet combustion procedure, and found to contain radioactivity to an extent accounting for an additional 24% of that known to be present. A solid residue remaining after the above wet combustion was filtered and re-assayed in the same way, accounting for an additional 11% of the radioactivity in no. 5, Table II. These results suggest that the thermal desorption process for Raney nickel samples containing adsorbed hydrogen and carbon monoxide not only involves conversion of the latter to methane, as discussed above, but also conversion to some quite refractory form of carbon, possibly a carbon–nickel alloy. This question is under further investigation.

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

Pyrolysis of Esters. XVII. Effect of Configuration on the Direction of Elimination[1]

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Vapor-phase chromatography showed that the pyrolysate from methyl *cis*-2-acetoxycyclohexanecarboxylate contained only methyl 2-cyclohexenecarboxylate and no methyl 1-cyclohexenecarboxylate. Similarly, the pyrolysate from the methyl *trans*-2-acetoxycyclohexanecarboxylate contained 97% of the conjugated ester and only 3% of the unconjugated isomer. Thus it appears that no *trans* elimination occurred in this cyclic system. Additional evidence that no rearrangement occurs during pyrolysis was obtained from the fact that pyrolysis of methyl 3-acetoxycyclohexanecarboxylate gave a mixture of methyl 2- and 3-cyclohexenecarboxylates but no conjugated ester.

Since Hurd and Blunck[3] proposed that esters pyrolyze by a unimolecular cyclic mechanism, evidence that supports this proposal has accumulated. One of the most convincing pieces of evidence is the demonstration that γ-lactones that can not sterically form an intermediate six-membered ring are stable at 600°, while larger lactones that can form a transient six-membered ring pyrolyze normally at 500°.[4] Alexander and Mudrak[5] showed also that in five- or six-membered cyclic systems *cis* elimination occurred more readily than did *trans* elimination. While both the *cis*- and *trans*-2-methylindanyl acetates gave the same product, 2-methylindene, a temperature approximately 200° higher was required for decomposition of the *trans* isomer. Similarly, pyrolysis of *cis*-2-phenylcyclohexyl acetate gave by a normal *cis* elimination 93% of 3-phenylcyclohexene but by an apparent *trans* elimination 7% of 1-phenylcyclohexene. The mechanism of this *trans* elimination is still a matter of speculation. Of course, Blomquist and Goldstein[6] showed that, if the ring was large enough, a so-called *trans*-hydrogen could be eliminated by a normal cyclic process.

Bordwell, *et al.*,[7] recently have shown that, if the activation of the hydrogen atom is great enough, ionic elimination reactions that normally proceed by way of a *trans* mechanism can be made to proceed through a *cis* mechanism. More recently, Bordwell and Landis[8] have shown that, if the *trans* hydrogen is sufficiently activated, the Chugaev elimination proceeds in a *trans* manner. It, therefore, seemed possible that, if the activation of the hydrogen atom was great enough, a *trans* elimination might take place during vapor-phase ester pyrolysis. In fact, a study of models showed that a transient six-membered ring was possible in a *trans* arrangement of the ester group and the hydrogen atom if the two groups were both equatorial and impossible if the two groups were both axial. Earlier work had shown that a carboxy group has a strong directional influence on the elimination so that pyrolysis of a β-acetoxybutyric ester produced almost exclusively the conjugated olefin.[9] It seemed possible, therefore, that pyrolysis of methyl *cis*-2-acetoxycyclohexanecarboxylate (I) might give rise to some *trans* elimination.

Mousseron and Canet[10] pyrolyzed both ethyl *cis*- and *trans*-2-acetoxycyclohexanecarboxylates (as well as the corresponding xanthates) and reported, as the only product, the conjugated olefin, ethyl 2-cyclohexenecarboxylate. Although the product suggests a *trans* elimination, the authors pointed out the possibility that the elimination might have proceeded by a normal *cis* elimination to produce the unconjugated olefin IV which then isomerized to the more stable conjugated olefin III.

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[1] Previous paper in this series, THIS JOURNAL, **81**, 651 (1959).

[2] Office of Naval Research Fellow, 1955–1957; Goodyear Tire and Rubber Co. Fellow, 1957–1958.

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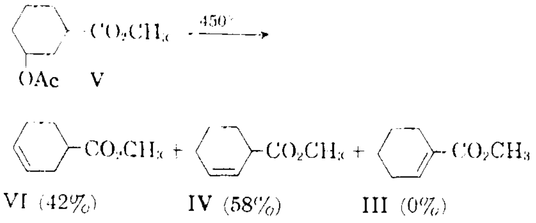
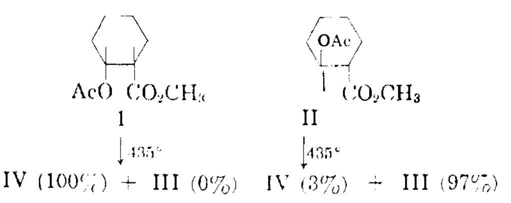
Recent work in this Laboratory[11] has shown that under carefully controlled conditions no rearrangement occurs during pyrolysis even with isomers of aromatic compounds. It seemed likely, therefore, that any rearrangement of the initial product could be prevented in the pyrolysis of the esters I and II. It seemed imperative to demonstrate



V

VI (42%) IV (58%) III (0%)



I II

IV (100%) + III (0%) IV (3%) + III (97%)

that the unconjugated ester IV would not isomerize to the conjugated ester III under the conditions of pyrolysis. In many cases described in the literature evidence that an olefin did not isomerize when it was dropped through the pyrolysis furnace was accepted as evidence that isomerization did not occur during ester pyrolysis. However, there is always a possibility that the experimental conditions are not the same in these two cases. It seemed a much surer procedure to synthesize the olefin independently by the pyrolysis of an isomeric ester under conditions at least as vigorous as those employed in the pyrolysis in question. Thus in order to establish whether methyl 3-cyclohexenecarboxylate (VI), if formed from the pyrolysis of I, would isomerize, methyl 3-acetoxycyclohexanecarboxylate (V) was prepared and pyrolyzed.

Hydrogenation of methyl *m*-hydroxybenzoate produced an 85% yield of a mixture of methyl *cis*- and *trans*-3-hydroxycyclohexanecarboxylate which was acetylated with acetic anhydride to give an 80% yield of corresponding 3-acetoxy compound V. Pyrolysis of V at 450° through a Vycor tube packed with Pyrex helices liberated 92% of the theoretical amount of acetic acid and produced a mixture of unsaturated esters. Vapor-phase chromatographic analysis indicated the pyrolysate consisted of a mixture of methyl 2- and 3-cyclohexenecarboxylates (IV and VI) with no methyl 1-cyclohexenecarboxylate (III). Infrared analysis indicated further that the mixture consisted of 58% of the 2-isomer IV and 42% of the 3-isomer VI.

For the two analyses the three possible unsaturated esters, III, IV and VI, were synthesized separately. A Diels–Alder reaction of butadiene and methyl acrylate produced the methyl 3-cyclohexenecarboxylate (VI). Bromination of cyclohexanecarboxylic acid, followed by treatment of the product with methanol, gave the methyl 1-bromocyclohexanecarboxylate. Subsequent treatment of the bromo ester with *sym*-collidine gave the desired methyl 1-cyclohexenecarboxylate (III). The methyl 2-cyclohexenecarboxylate (IV) was prepared by the pyrolysis of methyl *cis*-2-acetoxycyclohexanecarboxylate (I). These three unsaturated esters were used as standards for the vapor-phase chromatographs and infrared analyses.

Since it was established that no rearrangement of the unsaturated IV or VI to the conjugated isomer III occurred during pyrolysis at 450°, the syntheses and pyrolyses of the methyl *cis*- and *trans*-2-acetoxycyclohexanecarboxylates were undertaken. A Diels–Alder reaction between 1-acetoxy-1,3-butadiene and methyl acrylate gave an 80% yield of a mixture of adducts from which the solid methyl *cis*-2-acetoxy-3-cyclohexenecarboxylate could be crystallized in an over-all yield of 29%. Catalytic reduction of this unsaturated ester gave the desired methyl *cis*-2-acetoxycyclohexanecarboxylate (I) in a 62% yield. Pyrolysis of the *cis*-acetate I at 435° liberated 60% of the theoretical amount of acetic acid. Vapor-phase chromatography of the pyrolysate showed only a single peak corresponding to the methyl 3-cyclohexenecarboxylate (IV), with no evidence of the presence of the conjugated isomer III.

Catalytic reduction of methyl salicylate gave a 54% yield of a mixture of the methyl *cis*- and *trans*-2-hydroxycyclohexanecarboxylate, which was hydrolyzed and isomerized to give a 38% yield of the solid *trans*-2-hydroxycyclohexanecarboxylic acid. Acetylation, followed by esterification with diazomethane, gave the desired methyl *trans*-2-acetoxycyclohexanecarboxylate (II). Pyrolysis of this *trans* ester at 435° liberated 84% of the theoretical amount of acetic acid. A vapor-phase chromatograph indicated that the unsaturated portion of the pyrolysate consisted of 97% of conjugated isomer III and only 3% of the unconjugated isomer IV.

It must be concluded that under ideal conditions no rearrangement takes place during such a pyrolysis, even though a tendency to form the conjugated isomer exists. It also is obvious that the activation supplied by a carbomethoxy group is not sufficient to promote a *trans* elimination in spite of the fact that models show that the *trans* hydrogen can get very close to the carbonyl group. It appears that under the conditions (liquid-phase pyrolysis) employed by Mousseron and Canet[10] the *cis* ester underwent a *cis* elimination to produce the unconjugated ester IV, which subsequently rearranged to the conjugated isomer III. Very likely the *trans* eliminations observed by Alexander and Mudrak[5] proceeded through a mechanism much different from that usually assigned to ester pyrolysis. The possibility remains that the presence of a group that would activate the *trans* hydrogen more than a carbomethoxy group would promote a *trans* elimination during the pyrolysis of a carboxylic ester.

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(11) W. J. Bailey and J. Rosenberg, THIS JOURNAL, **77**, 73 (1955); W. J. Bailey, J. Rosenberg and L. J. Young, *ibid.*, **77**, 1163 (1955); W. J. Bailey, R. L. Hudson and C.-W. Liao, *ibid.*, **80**, 4358 (1958).

Experimental[12]

Methyl 3-Hydroxycyclohexanecarboxylate.—A mixture of 139 g. (0.915 mole) of methyl *m*-hydroxybenzoate, m.p. 71–73° (reported[13] m.p. 68–70°), 110 ml. of absolute alcohol and 5 g. of Raney nickel catalyst was hydrogenated at 180° and 240 atmospheres. After 80 minutes, the pressure drop was 100 atmospheres (measured at room temperature). The catalyst was removed by filtration and the filtrate was distilled through a 6-inch, helix-packed column to give 128 g. (85%) of a liquid mixture of methyl *cis*- and *trans*-3-hydroxycyclohexanecarboxylate, b.p. 134–146° (19 mm.), n^{25}D 1.4667 [reported b.p. 140–150° (14 mm.)[14]; *trans* isomer[15] b.p. 129–130° (12 mm.), n^{25}D 1.4660].

Methyl 3-Acetoxycyclohexanecarboxylate (V).—To 200 g. (2.0 moles) of refluxing acetic anhydride, a mixture of 127 g. (0.80 mole) of methyl 3-hydroxycyclohexanecarboxylate and 50 g. of acetic acid was added dropwise. When the addition was completed, heating was continued for an additional 30 minutes. Distillation of the mixture through an 18-inch, helix-packed column gave 130 g. (80%) of methyl 3-acetoxycyclohexanecarboxylate (V), b.p. 86–87° (1.0 mm.), n^{25}D 1.4508.

Anal. Calcd. for $C_{10}H_{16}O_4$: C, 59.98; H, 8.05. Found: C, 60.28; H, 7.82.

Pyrolysis of Methyl 3-Acetoxycyclohexanecarboxylate (V).—In two portions a total of 51 g. (0.25 mole) of methyl 3-acetoxycyclohexanecarboxylate was pyrolyzed at a rate of 30 drops per minute in a vertical Vycor tube packed with $^1/_8$-inch Pyrex helices and externally heated at 450° with a Hoskins 303 A electric furnace, as previously described.[16] The pyrolysate, which was faintly yellow, was dissolved in ether and extracted several times with distilled water to remove the liberated acetic acid. (Titration of an aliquot portion of the aqueous washings with standard base showed that 92% of the theoretical amount of acetic acid was liberated.)

The ethereal solution was dried over anhydrous magnesium sulfate and distilled through a 12-inch, helix-packed column to give in nine fractions 24.6 g. (70.3%) of a mixture of methyl 2- and 3-cyclohexenecarboxylate (IV and VI), b.p. 47–48° (3.5 mm.), n^{25}D 1.4582–1.4587.

Anal. Calcd. for $C_8H_{12}O_2$: C, 68.57; H, 8.57. Found: C, 68.38; H, 8.62.

This mixture was analyzed in the Perkin–Elmer model 154 vapor fractometer on the "A" column at a temperature of 150° with the gas pressure at 20 lb. per square inch and a recording range of 4. Under these conditions the retention time for the liquid was about 24 min., but the curve was not symmetrical. It had a definite shoulder on one side, indicating that there were two compounds in the mixture.

Methyl 3-Cyclohexenecarboxylate (VI).—A mixture of 27 g. (0.5 mole) of butadiene and 43 g. (0.5 mole) of methyl acrylate was heated at 130° for 1.5 hr. in a 300-ml. steel hydrogenation vessel. After the apparatus had cooled, the contents were distilled at reduced pressure through a 20-inch Podbielniak column to give 21 g. (30%) of methyl 3-cyclohexenecarboxylate (VI), b.p. 80–82° (23 mm.), n^{25}D 1.4575 [reported b.p. 116° (100 mm.),[17] n^{20}D 1.4602[17]; b.p. 72° (15 mm.),[18] n^{16}D 1.4635)[18]]. Vapor-phase chromatography showed a single peak with a retention time of 24 min. under the conditions described above.

Methyl *cis*-2-Acetoxy-3-cyclohexenecarboxylate.—A mixture of 74 g. (0.85 mole) of methyl acrylate, 95 g. (0.85 mole) of 1-acetoxy-1,3-butadiene[19] and 3.4 g. of N-phenyl-2-naphthylamine was heated with stirring at 80–105° for 13 hr., then at 130–150° for 5 hr., and finally at 165° for 5 hr. The resulting liquid was distilled through a Claisen head to give 135 g. (80%) of water-white liquid, b.p. 82–83° (0.7 mm.), which partially crystallized in the receiver. The solid that formed was removed by filtration and recrystallized from petroleum ether to produce 48 g. (29%) of pure methyl *cis*-2-acetoxy-3-cyclohexenecarboxylate,[20] m.p. 44.5–46.5°.

Anal. Calcd. for $C_{10}H_{14}O_4$: C, 60.60; H, 7.12. Found: C, 60.83; H, 7.07.

Methyl *cis*-2-Acetoxycyclohexanecarboxylate (I).—A mixture of 48 g. (0.24 mole) of methyl *cis*-2-acetoxy-3-cyclohexanecarboxylate, 40 ml. of acetic acid and 0.09 g. of Adams catalyst (PtO_2) was hydrogenated at room temperature and atmospheric pressure. A total of about 7.2 liters (136%) of hydrogen was absorbed. The catalyst was removed by filtration, and the filtrate was distilled through a 6-inch, helix-packed column to give 37 g. (76%) of methyl *cis*-2-acetoxycyclohexanecarboxylate (I),[20] b.p. 85.5° (1.3–1.4 mm.), n^{24}D 1.4487 [reported[10] b.p. 97–100° (3 mm.), n^{25}D 1.4497].

Anal. Calcd. for $C_{10}H_{16}O_4$: C, 59.99; H, 8.06. Found: C, 60.28; H, 7.90.

Pyrolysis of Methyl *cis*-2-Acetoxycyclohexanecarboxylate (I).—At a rate of about 24 drops per min., 28.0 g. (0.14 mole) of methyl *cis*-2-acetoxycyclohexanecarboxylate (I) was pyrolyzed at 435°, under the conditions described above. No charring was visible in the pyrolysis tube. The water-white pyrolysate was dissolved in ether and the resulting solution was extracted several times with distilled water. (Titration of an aliquot of the combined extracts with standard base showed that 60% of the theoretical amount of acetic acid had been liberated.) Distillation of the dried ethereal solution gave 11.0 g. (58%) of a liquid unsaturated ester, b.p. 78–80° (20 mm.), n^{25}D 1.4593.

With the conditions and apparatus described above, analysis by vapor-phase chromatography of this pyrolysate gave a single peak with a retention time of 25 min. Since there was only a single peak and the corresponding retention time for isomeric methyl 1-cyclohexenecarboxylate (III) was 39.5 min., it can be assumed that pyrolysis of methyl *cis*-2-acetoxycyclohexanecarboxylate (I) produced only methyl 2-cyclohexenecarboxylate (IV) and none of the conjugated isomer III.

Methyl 1-Bromocyclohexanecarboxylate.—Cyclohexanecarboxylic acid (75 g., 0.59 mole) was treated with 75 g. of thionyl chloride with cooling. When the addition was complete, the mixture was heated on the steam-bath for 2 hr. Bromine was added to the mixture heated at 80–90° for an additional 2 hr. By the use of a Claisen distilling head the mixture was heated on the steam-bath to remove the excess thionyl chloride. The dark, oily solution was then added to 75-ml. of anhydrous methanol with efficient stirring and cooling. After the addition was complete, the mixture was heated under reflux for 1 hr.

The reaction mixture was then poured into an ice–water mixture to produce a dark, oily layer. The oily liquid was separated from the water, and the aqueous layer was extracted with several portions of a 2% sodium bisulfite solution, a 5% sodium bicarbonate solution and finally with distilled water. The ethereal solution was dried over anhydrous magnesium sulfate and then distilled to yield 56 g. (43%) of methyl 1-bromocyclohexanecarboxylate, b.p. 34–35° (0.15 mm.), n^{25}D 1.4892–1.4896.

Methyl 1-Cyclohexenecarboxylate (III).—To 56 g. (0.25 mole) of methyl 1-bromocyclohexanecarboxylate was added dropwise 35 g. of *sym*-collidine while the mixture was kept cold. A brown precipitate formed. After the addition was complete, the mixture was heated under reflux for an additional 4 hr. After the mixture was cooled, about 100 ml. of ether was added and the mixture was heated under reflux for 15 min. The precipitate was removed by filtration to give about 51 g. (100%) of *sym*-collidine hydrobromide. The ethereal solution was washed with two 50-ml. portions of a 2% potassium bicarbonate solution, a 3% sulfuric acid solution and then distilled water. The solution was dried over magnesium sulfate and then distilled to

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[12] The authors are grateful to Miss Kathryn Gerdeman and Miss Jane Swan for the microanalyses and to Miss Kathryn Gerdeman for the infrared spectra. The infrared spectra were determined on the pure liquids with a Beckman IR-4 spectrometer. All melting points are corrected.

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[19] W. J. Bailey and R. Barclay, Jr., *J. Org. Chem.*, **21**, 328 (1956).

[20] The authors are indebted to Dr. Robert Barclay, Jr., for the preparation of this compound.

yield 15.3 g. (43%) of methyl 1-cyclohexenecarboxylate (III), b.p. 86.0° (15 mm.), n^{25}_{D} 1.4722 (reported[21] b.p. 193.5–195.5°). Analysis by vapor-phase chromatography of this sample of III under the conditions described above gave a single unsymmetrical peak with a retention time of 39.5 min.

Methyl 2-Hydroxycyclohexanecarboxylate.—A mixture of 100 g. (0.66 mole) of freshly distilled methyl salicylate, 100 ml. of methanol and 8 g. of Raney nickel was hydrogenated at 240 atmospheres and 180°. At the end of 4.5 hr. there was a 130-atmosphere pressure drop (measured at 25°). The catalyst was removed by filtration and the filtrate was distilled through a 6-inch, helix-packed column. After the methanol was removed, a two-phase liquid was collected. The residue was dissolved in ether and the solution was extracted with several portions of water. The ethereal solution was dried over magnesium sulfate and then distilled through a 6-inch, helix-packed column to give a low boiling fraction which separated into two layers, 25 g. of a forerun and 56.3 g. (54%) of a mixture of methyl *cis*- and *trans*-2-hydroxycyclohexanecarboxylate, b.p. 92–113° (7 mm.), n^{25}_{D} 1.4630–1.4637 [reported[22] for *cis* isomer, b.p. 105° (14 mm.), n^{25}_{D} 1.4640].

***trans*-2-Hydroxycyclohexanecarboxylic Acid.**—A hot solution of 80 g. of sodium hydroxide in 32 ml. of water and 87.0 g. (0.55 mole) of methyl 2-hydroxycyclohexanecarboxylate was allowed to stand overnight. A solution containing 40 g. of sodium hydroxide in 500 ml. of water was added to the mixture, and the resulting solution was heated under reflux for 36 hr. After the liquid was allowed to cool, it was made acid to congo red, then saturated with ammonium sulfate, and the resulting solution was extracted with ether. The combined organic extracts were dried over magnesium sulfate and the ether was removed by evaporation. The solid residue was recrystallized several times from ethyl acetate to give 30 g. (38%) of pure *trans*-2-hydroxycyclohexanecarboxylic acid, m.p. 108–109° (reported[22] m.p. 111°).

***trans*-2-Acetoxycyclohexanecarboxylic Acid.**—To a solution containing 29.8 g. (0.21 mole) of *trans*-2-hydroxycyclohexanecarboxylic acid in 300 ml. of freshly distilled pyridine was added 90 g. (1.15 moles) of acetyl chloride with stirring and efficient cooling. The mixture was neutralized with 30% sulfuric acid until it was acid to congo red and then it was extracted several times with ether. The combined organic extracts were dried over anhydrous magnesium sulfate and the ether was removed by distillation to give a white solid. Repeated recrystallization from ethyl acetate gave 13.6 g. (35%) of *trans*-2-acetoxycyclohexanecarboxylic acid, m.p. 102–103° (reported[22] m.p. 104.5–105.5°).

Methyl *trans*-2-Acetoxycyclohexanecarboxylate (II).—An ether solution containing 11.0 g. (0.059 mole) of *trans*-2-acetoxycyclohexanecarboxylic acid was treated with a solution of diazomethane (0.07 mole) in ether with gentle stirring while the reaction flask was maintained at 0°. After the addition was complete, the solution was allowed to stand overnight at room temperature. The solution was dried over anhydrous magnesium sulfate and distilled to yield 6.5 g. (55%) of methyl *trans*-2-acetoxycyclohexanecarboxylate (II), b.p. 86–87° (1.3 mm.), n^{25}_{D} 1.4474.

Anal. Calcd. for $C_{10}H_{16}O_4$: C, 59.98; H, 8.05. Found: C, 59.97; H, 8.24.

Pyrolysis of Methyl *trans*-2-Acetoxycyclohexanecarboxylate (II).—At a rate of 26 drops per min., 6 g. (0.03 mole) of methyl *trans*-2-acetoxycyclohexanecarboxylate (II) was pyrolyzed at 435°, according to the procedure described above. The pyrolysis tube showed only slight charring where the drops of liquid hit the glass helices. The water-white pyrolysate was dissolved in ether and washed several times with distilled water. (Titration of an aliquot of the combined aqueous washings showed that 84% of the theoretical amount of acetic acid had been liberated.) The ethereal solution was dried over anhydrous magnesium sulfate and distilled through a 20-inch Podbielniak column to give 3 g. of liquid, b.p. 86–89° (19 mm.), n^{25}_{D} 1.4723.

A vapor-phase chromatographic analysis under the conditions described above gave two unsymmetrical curves having retention times of 25.4 and 38.4 min. The ratio of each isomer in the sample was determined by weighing the areas under each curve. A sample analysis of a synthetic mixture of the same two isomers by this procedure and under the same conditions showed that it was accurate to approximately 1%. The ratio of methyl 1-cyclohexenecarboxylate (III) to methyl 3-cyclohexenecarboxylate (IV) obtained in this manner from the pyrolysis of methyl *trans*-2-acetoxycyclohexanecarboxylate (II) was 97 to 3.

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