× 300 mm. borosilicate glass combustion tube that was packed with $^1/_{16}$-inch helices. The tube was continuously swept out with dry, oxygen-free nitrogen and externally heated at 500° with a 12-inch Hoskins furnace.[7] The pyrolysate was condensed in a 6-inch spiral condenser and then collected in a receiver immersed in a Dry Ice–acetone-bath. The pyrolysate was washed with water and dried over anhydrous potassium carbonate. Titration of aliquots of the washings indicated that 71% of the total theoretical acetic acid had been liberated. The pyrolysate was fractionated through a 16 × 1.7 cm. column, packed with $^1/_8$-inch helices, to yield 68.1 g. (47%) of 1,2-dimethylene-4-cyclohexene (I), b.p. 90° (100 mm.), n^{22}D 1.4968, d^{25}_4 0.8692; 66.0 g. (30%) of 2-methylene-Δ^4-tetrahydrobenzyl acetate (V); and 56.4 g. (19%) of recovered diacetate IV. The total yield of 1,2-dimethylene-4-cyclohexene (I), based on unrecovered diacetate IV and olefin acetate V was 92%. The recovered IV and V could be pyrolyzed separately to produce additional I.

Anal. Calcd. for C_8H_{10}: C, 90.50; H, 9.50. Found: C, 90.68; H, 9.68.

Catalytic Isomerization of 1,2-Dimethylene-4-cyclohexene (I).—A mixture of 3.0 g. (0.028 mole) of 1,2-dimethylene-4-cyclohexene (I) and 0.5 g. of palladium-on-charcoal was heated under reflux for 48 hours. The mixture was filtered to give 2.9 g. (97%) of *o*-xylene, n^{25}D 1.5066. One gram (0.0094 mole) of this filtrate was oxidized with alkaline potassium permanganate, according to the directions of Shriner and Fuson,[13] to yield 1.48 g. (94%) of phthalic acid, m.p. 208°, which showed no depression in its melting point when it was mixed with authentic phthalic acid.

Acid Isomerization of 1,2-Dimethylene-4-cyclohexene (I).—In order to test the stability of the 1,2-dimethylene-4-cyclohexene (I) to acetic acid, which is formed in the pyrolysis, 5 g. of the triene I was refluxed with 100 ml. of anhydrous glacial acetic acid for 2 hours and was recovered unchanged. However, if a drop of concentrated hydrochloric acid was added to the mixture, an immediate reaction took place. Distillation of the reaction mixture produced 1.1 g. of *o*-xylene, with no recovered triene I; a polymeric substance remained as the residue in the flask.

1,4,5,8-Tetrahydronaphthalene-2,3-dicarboxylic Acid (VI).—A solution of 5.7 g. (0.05 mole) of acetylenedicarboxylic acid in 50 ml. of benzene was heated under reflux in a 100-ml., three-necked flask, equipped with a stirrer, a dropping funnel, and a condenser. After 5.3 g. (0.05 mole) of 1,2-dimethylene-4-cyclohexene (I) was added dropwise with stirring, the mixture was allowed to stand for 24 hours. The precipitate was filtered off and the filtrate was concentrated. The concentrate was diluted with petroleum ether to produce an additional quantity of material. Recrystallization of the adduct from acetic acid gave 9.2 g. (84%) of 1,4,5,8-tetrahydronaphthalene-2,3-dicarboxylic acid (VI), m.p. 200–201°.

Anal. Calcd. for $C_{12}H_{12}O_4$: C, 65.45; H, 5.45. Found: C, 65.28; H, 5.32.

An intimate mixture of 0.2 g. of the adduct VI, 0.1 g. of 5% palladium-on-charcoal, and 0.05 g. of copper chromite was placed in a dehydrogenation apparatus. The system was flushed with carbon dioxide, the mixture was heated at 270°, and 43.0 ml. (90%) of hydrogen was collected. The solid (0.1 g.) that sublimed to the cold finger melted at 80° and no depression of its melting point was observed when it was mixed with an authentic sample of naphthalene.

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

Pyrolysis of Esters. I. Selectivity in the Direction of Elimination by Pyrolysis[1]

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When unsymmetrical secondary esters were pyrolyzed under mild conditions, it was found that the dehydroacetoxylation proceeded in a highly selective manner to give only a single olefin following the Hofmann rule. Many uses of this new synthetic tool are outlined.

Because olefins are widely used as monomers for polymerization and reactive chemical intermediates, their syntheses through elimination reactions have been studied thoroughly. One particular problem that has attracted interest has been the direction of the elimination when two olefins are possible.[4] The Hofmann rule states that in the decomposition of a quaternary ammonium hydroxide the major product will be that olefin having the smallest number of attached alkyl groups. The Saytzeff rule states that when an alkyl halide is converted to an olefin the major product will be the most highly branched olefin. Ingold[5] found, however, that with ammonium and sulfonium ions the Hofmann rule was followed only if the reaction involved second-order kinetics. In all other elimination reactions which he studied, including the dehydration of alcohols, the Saytzeff rule predominated. His work further emphasized that a mixture of products was obtained in each elimination reaction.

Brown and Moritani[6] have recently shown that with base-catalyzed dehydrohalogenation the Saytzeff rule is followed only in the very simple cases, and the product of the reaction is governed by the steric requirements of the base. With the 2-bromo-3-methylbutane they were able to change the amount of 3-methyl-1-butene from 29% using sodium ethoxide to 66% using potassium *t*-butoxide. Thus it appears that, except for highly strained molecules, first-order elimination reactions tend to follow the Saytzeff rule but bimolecular elimination reactions may follow either rule, depending on the steric nature of the groups or reagent.

The pyrolysis of esters is an excellent method for the introduction of unsaturation. It was shown in this Laboratory that the highly strained 1,2-dimethylene-4-cyclohexene, which is an isomer of *o*-

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(4) E. R. Alexander, "Principles of Ionic Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1950, p. 113.

(5) E. D. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953.

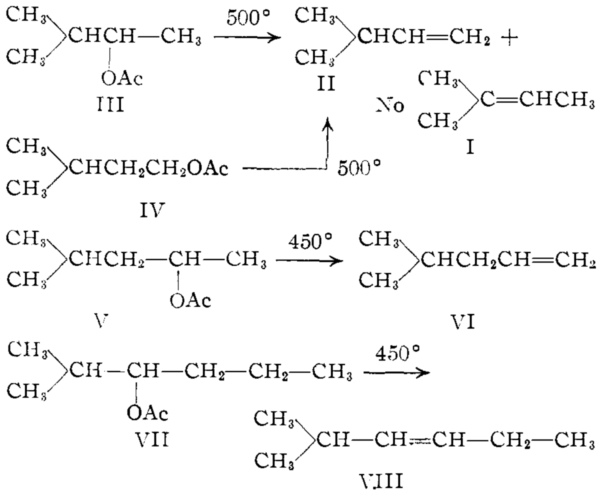
(6) H. C. Brown and I. Moritani, THIS JOURNAL, **75**, 4112 (1953).

xylene, could be synthesized in a 92% yield with no rearrangement by the pyrolysis of a diacetate.[7] Because of the ready accessibility of esters, the ease of carrying out the pyrolysis,[8] the high yield and purity of the product, the lack of rearrangements and the saving of time and materials, a research program has been undertaken to determine the scope of this interesting reaction.

It was of interest, therefore, to determine how the pyrolysis of esters fits into the pattern of the elimination reactions mentioned above in regard to the direction of elimination of the molecule of acid. It had been shown that the pyrolysis of esters proceeds by an intramolecular *cis* elimination[9] while the reactions discussed above proceed by a *trans* elimination.

Methylisopropylcarbinyl acetate (III) therefore was pyrolyzed at 500° under such conditions that only 77% of the acetic acid was eliminated. These conditions were chosen so as to make sure that no carbonization took place which might cause rearrangement of the product.[7] When the pyrolysate was worked up, only 3-methyl-1-butene (II) was obtained. No 2-methyl-2-butene (I) was detected, even though the two olefins differ in boiling point by 17° and in $n^{20}\text{D}$ by over 0.0200. The purity of II was indicated by an independent synthesis by the pyrolysis of isoamyl acetate. The two samples apparently possessed identical refractive indices and infrared absorption spectra.

Since the result of this one pyrolysis was so surprising, an attempt was made to determine whether this phenomenon was general. In the pyrolysis of III, the hydrogen was removed from the methyl group in preference to the methynyl group. It was, therefore, of interest to study the pyrolysis of esters where the choice of the hydrogen to be abstracted was between a tertiary and a secondary and between a secondary and a primary. When methylisobutylcarbinyl acetate (V) was pyrolyzed, the Hofmann rule was followed and again only one product was isolated, the 4-methyl-1-pentene (VI). However, since the physical properties of VI and the isomeric 4-methyl-2-pentene differ only moderately, it can only be said that within the limit of accuracy of the method used the VI obtained by pyrolysis is at least 95% pure. When *n*-propylisopropylcarbinyl acetate (VII) was pyrolyzed, again only a single product, 2-methyl-3-hexene (VIII), resulting from the abstraction of the secondary hydrogen, was found. For the same reasons, the sample of VIII was at least 95% pure.



It thus appears that all simple secondary aliphatic acetates undergo pyrolytic dehydroacetoxylation according to the Hofmann rule. The surprising thing about these pyrolyses is that in each case only one product was obtained. This sets the pyrolysis of esters apart from acid- or base-catalyzed elimination reactions which almost always produce a mixture of olefins. Of course it had been previously demonstrated that under proper experimental conditions no rearrangement of the olefins occurs in the pyrolysis tube.[7,9a,10] Several explanations can be offered to account for the formation of the least highly alkylated olefin in pyrolysis, but none will satisfactorily explain the high selectivity. If the reaction involves the nucleophilic displacement of the carbonyl oxygen on the hydrogen, the inductive effect of alkyl groups attached to the same carbon would hinder the reaction. On this basis, it would be predicted that the hydrogens would be abstracted in the order: primary > secondary > tertiary. This order would be aided by the statistical effect of the greater number of primary hydrogens as well as the lower steric requirement of these primary hydrogens. However, none of these considerations would predict the production of a single olefin. The fact that the temperature of the pyrolysis is much higher than for most other elimination reactions suggests that the effect of temperature on the products of the ionic reactions be studied.

Since the direction of elimination in pyrolysis is in general opposite to that of the simple dehydration of secondary alcohols, a new synthetic tool is available. The fact that secondary alcohols are very often easily accessible chemical intermediates suggests many convenient syntheses of olefins and monomers that are difficult to prepare by conventional methods. For example, the synthesis of 4-methyl-1-pentene (VI) from the readily available methylisobutylcarbinol probably represents the most convenient method of preparation of that olefin.

Research designed to determine the effect of structural changes on the direction of elimination and to apply this new synthetic tool to the preparation of new monomers is in progress in this Laboratory.

Experimental[11]

Methylisopropylcarbinyl Acetate (III).—Methylisopropylcarbinol was prepared from isopropylmagnesium bromide and acetaldehyde in 50% yield and distilled through a 6-inch, helix-packed column to obtain the pure carbinol, b.p. 108–110° (742 mm.), $n^{20}\text{D}$ 1.4067 (reported[12] b.p. 111–112°).

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[11] All temperature readings are uncorrected.

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Esterification of the carbinol with acetic anhydride followed by fractionation of the product through a 6-inch, helix-packed column produced a 72% yield of methylisopropylcarbinyl acetate (III), b.p. 128–129° (742 mm.), n^{20}_{D} 1.3958 [reported[12b] b.p. 128.5–129° (758 mm.), n^{25}_{D} 1.3932].

3-Methyl-1-butene (II). A. By Pyrolysis of Methylisopropylcarbinyl Acetate (III).—The apparatus used for pyrolysis consisted of a Vycor tube, 3 cm. in diameter and 55 cm. in length, inserted in a 12-inch FD303A Hoskins electric furnace. The tube was packed for 25 cm. of its length with $^1/_8$-inch Pyrex helices. Eighty grams (0.61 mole) of methylisopropylcarbinyl acetate (III) was placed in a 100-ml., round-bottom flask equipped with a side arm, which was connected to a source of compressed air that forced the liquid through a U-shaped capillary tube extending from the bottom of the flask to the top of the pyrolysis tube. A uniform rate of addition was effected by suitable adjustment of the air pressure; the most satisfactory dropping rate was about 1.5 ml. per minute. A slow stream (5 ml. per minute) of dried nitrogen was introduced through the top of the tube during pyrolysis. The nitrogen performed the twofold function of maintaining non-oxidizing conditions within the tube and of forcing the pyrolysate vapor into the receiver, a round-bottom flask equipped with a side arm. Interposed between the receiver, which was immersed in a Dry Ice–chloroform cold-bath, and pyrolysis tube was a short spiral water condenser. The pyrolysis was conducted at a temperature of 500°, as determined by a pyrometer and thermocouple attached to the outside of the pyrolysis tube. In order to minimize the possibility of any rearrangement taking place, extreme care was taken that the pyrolysis was conducted at such a rate and temperature that no noticeable carbonization occurred in the pyrolysis tube.

Fractionation of the pyrolysate through a 6-inch, helix-packed column yielded 20 fractions totaling 30.0 g. (70%) of 3-methyl-1-butene (II), b.p. 21–23° (749 mm.), n^{15}_{D} 1.3670–1.3690 [reported b.p. 21–23° (755 mm.),[13] n^{15}_{D} 1.3680[14]]; 28.1 g. (77%) of acetic acid; and 17 g. (21% recovery) of methylisopropylcarbinyl acetate (III). The isomeric 2-methyl-2-butene has a b.p. 38.2–38.4° (760 mm.),[15] n^{20}_{D} 1.3877.[15] Comparison of the infrared absorption spectrum of II with that of an authentic sample prepared from isoamyl acetate showed that the two samples were identical.

B. By Pyrolysis of Isoamyl Acetate (IV).—By using the apparatus described above, 65 g. (0.5 mole) of isoamyl acetate (IV) was pyrolyzed at 500°. The pyrolysate was fractionated through a 6-inch, helix-packed column to yield 22 g. (63%) of 3-methyl-1-butene (II), b.p. 21–23° (745 mm.), n^{15}_{D} 1.3672–1.3690; and 22 g. (34% recovery) of isoamyl acetate.

Methylisobutylcarbinyl Acetate (V).—Methylisobutylcarbinol was esterified with acetic anhydride and the product was distilled through a 12-inch, helix-packed column to produce a 74% yield of methylisobutylcarbinyl acetate (V), b.p. 143–145° (730 mm.), n^{20}_{D} 1.3980 (reported[16] b.p. 147–148°).

Pyrolysis of Methylisobutylcarbinyl Acetate (V).—Seventy-two grams (0.5 mole) of methylisobutylcarbinyl acetate (V) was pyrolyzed as described above at 450° over a period of 65 minutes. Extraction of the pyrolysate with water, followed by titration of an aliquot with standard base, indicated that 54% of the theoretical acetic acid had been cracked out. The organic layer was dried over magnesium sulfate and fractionated through a 6-inch, helix-packed column to yield twenty fractions, amounting to 20.3 g. (48%) of 4-methyl-1-pentene (VI), b.p. 53–54° (745 mm.), n^{20}_{D} 1.3820–1.3835 [reported b.p. 54.0–54.1° (760 mm.),[17] n^{20}_{D} 1.3825,[18] n^{25}_{D} 1.3839[19]]. Reported[17] constants for the isomeric 4-methyl-2-pentene are b.p. 58.6–59.1° (760 mm.), n^{20}_{D} 1.3869.

***n*-Propylisopropylcarbinyl Acetate (VII).**—*n*-Propylisopropylcarbinol, b.p. 141–145° (752 mm.), n^{25}_{D} 1.4160 [reported[20] b.p. 144–145° (734 mm.), n^{20}_{D} 1.4113)] was prepared in a 68% yield by the reaction of isopropylmagnesium bromide with *n*-butyraldehyde followed by fractionation of the product through a 12-inch helix-packed column. Esterification of the carbinol with acetic anhydride and subsequent distillation through a 12-inch, helix-packed column produced a 91% yield of *n*-propylisopropylcarbinyl acetate (VII), b.p. 164–166° (750 mm.), n^{25}_{D} 1.4072 [reported[21] b.p. 162–163° (765 mm.)].

Pyrolysis of *n*-Propylisopropylcarbinyl Acetate (VII).—Seventy-nine grams (0.5 mole) of propylisopropylcarbinyl acetate (VII) was pyrolyzed at 450° as described above, over a period of 90 minutes. Extraction of the pyrolysate with water, followed by titration of an aliquot of the aqueous layer with base, indicated that 83% of the acetic acid was cracked out. The organic layer was dried over sodium sulfate and fractionated through a 6-inch, helix-packed column to yield 38 g. (77%) of 2-methyl-3-hexene in twenty fractions, b.p. 83–85° (732 mm.), n^{20}_{D} 1.3990–1.4003 [reported[22] b.p. 85–86° (760 mm.), n^{20}_{D} 1.3991]. The corresponding properties[22] for the isomeric hydrocarbon, 2-methyl-2-hexene, are b.p. 94.4–94.6° (760 mm.), n^{20}_{D} 1.4075.

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