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

Pyrolysis of Esters. V. Mechanism of 1,4-Elimination[1]

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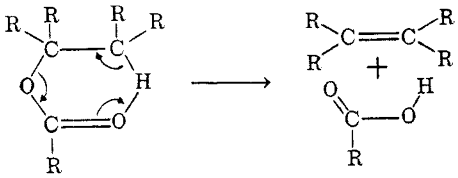
Received November 21, 1955

When either *cis*-1,4-diacetoxy-2-butene or 1,2-diacetoxy-3-butene is pyrolyzed to yield 1-acetoxy-1,3-butadiene, the recovered diacetate consists of a mixture of the 1,4- and the 1,2-diacetoxy compounds. This equilibrium between these allylic isomers plus the fact the 1,2-derivative pyrolyzed more easily than the 1,4-isomer suggest that the 1,4-diacetoxy-2-butene pyrolyzes by first undergoing a thermal allylic rearrangement to the 1,2-diacetoxy-3-butene, which subsequently decomposes by a quasi-six-membered ring to form the 1-acetoxy-1,3-butadiene.

When an ester containing a moderately active β-hydrogen is heated to a high temperature, cleavage takes place to form an olefin and an acid. The most probable mechanism for this cleavage involves a quasi-six-membered ring according to the following scheme:[3,4]



It also has been known for some time that crotyl esters and their derivatives that contain either an inactive β-hydrogen, or none at all, but a fairly active δ-hydrogen decompose to yield a diene plus an acid. For example, crotyl acetate on pyrolysis gives a good yield of butadiene plus acetic acid.[5,6] Pyrolysis of the acetate[7] or benzoate[8] of 1-hydroxy-1-cyano-2-butene leads to the formation of 1-cyano-1,3-butadiene. In some cases the elimination of the δ-hydrogen competes successfully with the simultaneous elimination of a β-hydrogen. Thus the pyrolysis of 1-cyclohexyl-3-acetoxy-1-butene gives a 41% yield of 1-cyclohexyl-1,3-butadiene as well as an 11% yield of 1-cyclohexylidine-2-butene.[9]

Three different mechanisms have been stated or implied in the literature for this 1,4-elimination during pyrolysis. Cristol, Barasch, and Tieman found that *trans*-9,10-diacetoxy-1,5-dichloro-9,10-dihydroanthracene, which has an acetoxy group and a δ-hydrogen *cis* to one another, readily lost a molecule of acetic acid at its melting point, while the corresponding *cis* isomer was stable under the same conditions. On this basis, they assumed that the molecule of acetic acid was eliminated by a direct *cis*-1,4-mechanism involving a quasi-eight-membered ring.[10] Schniepp and Geller[11] postulated that the crotyl esters decomposed initially by the usual β-elimination to form an allene which subsequently rearranged to the conjugated diene. Grummitt and Splitter[9] suggested that the crotyl esters first underwent an allylic rearrangement, followed by the normal β-elimination. None of the above postulates was supported by direct evidence and neither of the intermediates postulated in the latter two mechanisms was isolated.

The formation of the intermediate allene is not likely in view of the fact that simple allyl esters do not decompose under the conditions that give high yields of dienes from the crotyl esters. In fact, both allyl acetate and isopropenyl acetate decompose at much higher temperatures to form ketene rather than acetic acid.[12] It also has been shown that there is little or no tendency for the rearrangement of carbon-to-carbon double bonds during pyrolysis, provided that charring is eliminated.[13,14]

The direct 1,4-elimination involving an eight-membered ring may operate in some cases but it cannot be the preferred mechanism for the decomposition of all crotyl esters. It has been shown, for example, that 1-cyclohexenylmethyl acetate (I) can be pyrolyzed at 500° to form a 93% yield of 3-methylenecyclohexene (II).[15] Examination of models of the unsaturated ester I showed that an eight-membered ring involving the δ-hydrogen and the acetoxy group (structure Ia) was highly unlikely. Such a quasi ring would, in a sense, form a

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[1] Previous paper in this series, *J. Am. Chem. Soc.*, **77**, 2787 (1955).

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[3] Alexander and Mudrak, *J. Am. Chem. Soc.*, **72**, 1811 (1950).

[4] Hurd and Blunck, *J. Am. Chem. Soc.*, **60**, 2419 (1938); Arnold, Smith, and Dodson, *J. Org. Chem.*, **15**, 1256 (1950).

[5] Ostromysslenski, *Zhur. Russ. Fiz.-Khim. Obshchestva*, **47**, 1486 (1915).

[6] Morell, Geller, and Lathrop, *Ind. Eng. Chem.*, **37**, 877 (1945).

[7] Treppenhauer, German Patent 673,427 (1938) [*Chem. Abstr.*, **33**, 4272 (1939)].

[8] Snyder, Stewart, and Myers, *J. Am. Chem. Soc.*, **71**, 1055 (1949).

[9] Grummitt and Splitter, *J. Am. Chem. Soc.*, **74**, 3924 (1952).

[10] Cristol, Barasch, and Tieman, *J. Am. Chem. Soc.*, **77**, 583 (1955).

[11] Schniepp and Geller, *J. Am. Chem. Soc.*, **67**, 54 (1945).

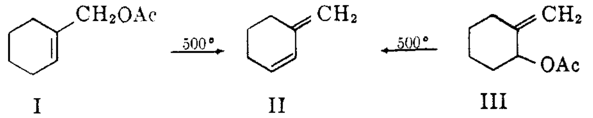
[12] Bailey and Young, unpublished work.

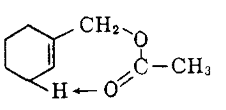
[13] Bailey and Rosenberg, *J. Am. Chem. Soc.*, **77**, 73 (1955).

[14] Bailey, Rosenberg, and Young, *J. Am. Chem. Soc.*, **77**, 1163 (1955).

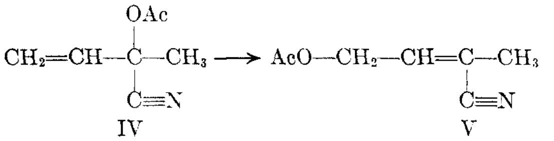
[15] Bailey and Goossens, *J. Am. Chem. Soc.*, **78**, in press (1956).

bicyclic intermediate with a double bond at an atomic bridgehead in violation of Bredt's rule. One must conclude, therefore, that the acetate I first rearranges to the acetate III which then can undergo normal β-elimination through an intermediate six-membered ring. The fact that 2-methylenecyclohexyl acetate (III) can be pyrolyzed to a high yield of 3-methylenecyclohexene (II) under almost the identical conditions that were used for the pyrolysis of I gives added substance to this conclusion.



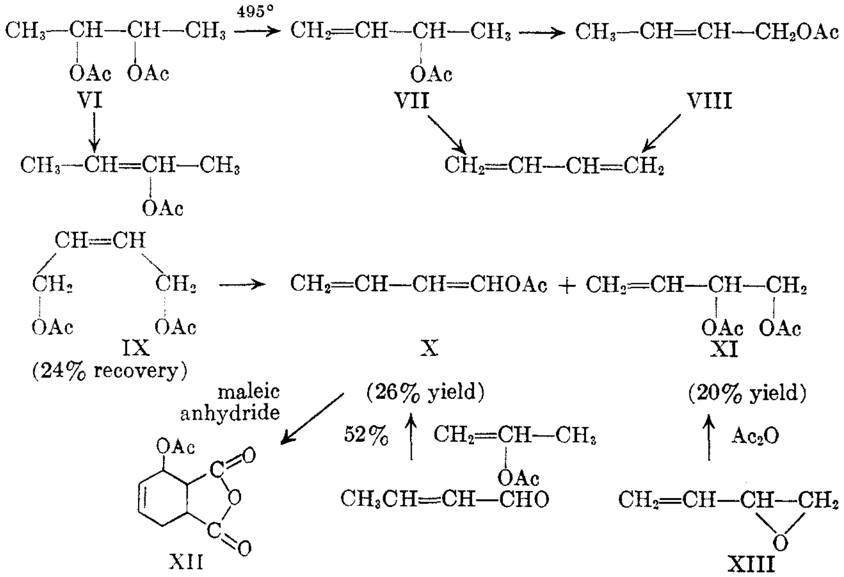


Ia



$$CH_2{=}CH{-}\overset{OAc}{\underset{C\equiv N}{C}}{-}CH_3 \longrightarrow AcO{-}CH_2{-}CH{=}\underset{C\equiv N}{C}{-}CH_3$$

IV V



Allylic rearrangements have been noted during the pyrolysis of unsaturated esters, but their role in the pyrolysis has not been established. Marvel and Brace[16] found that during the pyrolysis of 3-acetoxy-3-cyano-1-butene (IV) to obtain 2-cyano-1,3-butadiene some 1-acetoxy-3-cyano-2-butene (V) was formed. However, V did not pyrolyze under the same conditions that were used for the pyrolysis of IV to produce 2-cyanobutadiene. When Morell, Geller, and Lathrop[6] investigated the synthesis of butadiene from 2,3-diacetoxybutane (VI), they isolated, in addition to the butadiene, three unsaturated monoacetates, methylvinylcarbinyl acetate (VII), crotyl acetate (VIII) and 2-acetoxy-2-butene. One must conclude that the crotyl acetate (VIII) was formed by an allylic rearrangement of VII. Although both VII and VIII gave butadiene on further pyrolysis, no equilibrium or interconversion was shown for these isomeric esters. On the contrary, the fact that pyrolysis of the optically active diacetate VI gives optically active (although partially racemized) methylvinylcarbinyl acetate (VII)[17] suggests that there is no mobile equilibrium between VII and VIII during the pyrolysis.

No one has investigated the vapor-phase or noncatalyzed rearrangement of allylic esters. Young and Webb,[18] however, did study the liquid-phase isomerization of methylvinylcarbinyl acetate (VII) to crotyl acetate (VIII) and found that the reaction was first order and acid-catalyzed and very probably proceeds through an intermediate carbonium ion. This mechanism could not operate during the vapor-phase pyrolysis since it has been shown that this reaction has characteristics that differ markedly from an ionic elimination[19] and can be used for the synthesis of highly acid-sensitive strained dienes such as 1,2-dimethylene-4-cyclohexene, an isomer of *o*-xylene.[13]

A research program was designed, .therefore, to obtain more evidence for the allylic rearrangement of crotyl esters during pyrolysis. Since *cis*-2-butene-1,4-diol was commercially available, the corresponding diacetate IX was considered to be an ideal starting material for this study. The *cis* configuration of this ester should favor a direct 1,4-elimination if that mechanism is at all important in the pyrolysis of crotyl esters. Thus it was felt that if it

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(16) Marvel and Brace, *J. Am. Chem. Soc.*, **70**, 1775 (1948).

(17) Morell and Auernheimer, *J. Am. Chem. Soc.*, **66**, 792 (1944).

(18) Young and Webb, *J. Am. Chem. Soc.*, **73**, 780 (1951).

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

could be demonstrated that the elimination of acetic acid was preceded by an allylic rearrangement in the case of this *cis* ester, one would be justified in assuming that this same rearrangement takes place in *trans* crotyl esters such as I.

cis-1,4-Diacetoxy-2-butene (IX) was pyrolyzed by the addition of the liquid IX to a vertical Vycor tube packed with Pyrex helices and externally heated at 495°. The tube was continuously flushed with a slow stream of oxygen-free nitrogen to minimize charring. Under these conditions, 77% of one molar equivalent of acetic acid was liberated. From this pyrolysis were obtained a 26% yield of 1-acetoxy-1,3-butadiene (X), a 24% recovery of the starting diacetate IX, and a 20% yield of an isomeric 1,2-diacetoxy-3-butene (XI). The 1-acetoxy-1,3-butadiene (X) was identified by conversion to a solid derivative and comparison of its properties with an authentic sample prepared from crotonaldehyde and isopropenyl acetate. Maleic anhydride plus the X from the pyrolysis produced the known 3-acetoxy-1,2,3,6-tetrahydrophthalic anhydride (XII). The failure to isolate any of the high-melting isomeric 4-acetoxy-1,2,3,6-tetrahydrophthalic anhydride indicates the absence of any 2-acetoxy-1,3-butadiene from the pyrolysis products. The 1,2-diacetoxy-3-butene (XI) was identified by comparison of its infrared absorption spectrum with that of an authentic sample prepared from 1,2-epoxy-3-butene (XIII) and acetic anhydride. XI possessed strong absorption bands at 1045, 1216, 1356, and 1692 cm.$^{-1}$ and medium bands at 866, 940, 989, and 1121 cm.$^{-1}$. The isomeric starting diacetate IX had strong bands in the infrared at 1029, 1216, 1356, and 1704 cm.$^{-1}$ and medium bands at 838, 883, 965, and 1119 cm.$^{-1}$.

The fact that the two diacetates, IX and XI, were interconvertible in the vapor state was demonstrated by the results of the pyrolysis of XI. When 1,2-diacetoxy-3-butene (XI) was pyrolyzed under the identical conditions used for the pyrolysis of IX, 83% of one molar equivalent of acetic acid was liberated. From the pyrolysate were isolated a 29% yield of 1-acetoxy-1,3-butadiene (X), a 14% recovery of the starting diacetate XI, and a 6% yield of the isomeric 1,4-diacetoxy-2-butene (presumably a mixture of *cis* and *trans* isomers). The reaction products were identified in the manner described above.

The fact that 1,2-diacetoxy-3-butene (XI) pyrolyzes more easily than the isomeric 1,4-diacetoxy-2-butene (IX), coupled with the fact that there is an equilibrium between XI and IX during pyrolysis, indicates that XI is very probably an intermediate in the pyrolysis of IX. Thus it appears that the preferred mechanism for the pyrolysis of IX is the allylic rearrangement to XI, which then undergoes β-elimination by the usual process. The present results do not eliminate the possibility that a small amount of the *cis* ester IX undergoes a direct 1,4-elimination through an intermediate eight-membered ring. One must conclude, however, that the pyrolysis of the *trans* ester I very likely proceeds exclusively through an allylic rearrangement since a direct 1,4-elimination is highly improbable. Thus, if the allylic rearrangement is preferred over the direct 1,4-elimination in a case highly favorable to this direct mechanism, one can assume that the allylic rearrangement is a general mechanism for the pyrolysis of crotyl esters.

EXPERIMENTAL[20]

cis-1,4-Diacetoxy-2-butene (IX). To a mixture of 1285 g. (12.59 moles) of acetic anhydride and 60 g. (1.0 mole) of acetic acid, heated under reflux, was added dropwise 444 g. (5.04 moles) of *cis*-2-butene-1,4-diol (General Aniline and Film Corp.) over a period of 35 minutes. After the reaction mixture had been heated under reflux for 24 hours, the mixture was fractionated through a 6-inch, helix-packed column to yield 836 g. (96%) of *cis*-1,4-diacetoxy-2-butene (IX), b.p. 73–80° (1.1–1.5 mm.), n_D^{25} 1.4404 [reported[21] b.p. 120–121° (18 mm.), n_D^{19} 1.4435].

1-Acetoxy-1,3-butadiene (X). A modification of the methods of Hagemeyer and Hull[22] and Quattlebaum and Noffsinger[23] was found to be superior to other procedures for the preparation of pure acetoxybutadiene (X). A mixture of 676 g. (6.75 moles) of isopropenyl acetate, b.p. 97.0°, 8 g. of *p*-toluenesulfonic acid, and 2 g. of cupric acetate was placed in a 3-liter, three-necked flask, equipped with a 16-inch, helix-packed column, a stirrer, a dropping-funnel, and a thermometer extending into the liquid. While the reaction mixture was heated under reflux, 350 g. (5 moles) of freshly distilled crotonaldehyde, b.p. 101–103°, was added dropwise over a period of 5.75 hours. The acetone was removed from the reaction mixture through the column as fast as it was formed by the collection of all material boiling below 58° until 330 ml. (90%) of acetone had been collected. To the ice-cold reaction mixture were added 17 g. of triethanolamine and 1 liter of water, and the resulting two-phase system was distilled at 52–58 mm. The aqueous layer of the distillate was extracted with ether, and the extracts were combined with the organic portion of the distillate. After the combined solutions were washed twice with a 10% potassium carbonate solution, 5 g. of N-phenyl-β-naphthylamine was added and the mixture was dried over magnesium sulfate. Fractionation of this material through a 12-inch, helix-packed column produced 293 g. (52%) of 1-acetoxy-1,3-butadiene (X) b.p. 56.8–58.0° (37 mm.), n_D^{25} 1.4667 [reported[24] b.p. 42–43° (16 mm.), n_D^{20} 1.4687].

1,2-Diacetoxy-3-butene (XI). By use of the method of Whitmore and Krems,[25] 100 g. (1.43 moles) of freshly distilled 1,2-epoxy-3-butene, b.p. 66.4–67°, n_D^{22} 1.4158, was added dropwise over a period of 75 minutes to a mixture of 157 g. (1.54 moles) of acetic anhydride and 13 g. of sub-

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(20) The authors are indebted to Kathryn Gerdeman and Joseph Wenograd for the infrared absorption spectra. The spectra were determined with the pure liquids and with carbon disulfide solutions in a Perkin-Elmer Model 12-C spectrophotometer modified for double-pass operation. All melting points are uncorrected.

(21) Raphael, *J. Chem. Soc.*, 401 (1952).

(22) Hagemeyer and Hull, *Ind. Eng. Chem.*, **41**, 2920 (1949).

(23) Quattlebaum and Noffsinger, U. S. Patent 2,467,095 (1948) [*Chem. Abstr.*, **43**, 5795 (1949)].

(24) Wichterle and Hudlicky, *Collection Czechoslov. Chem. Commun.*, **12**, 564 (1947).

(25) Whitmore and Krems, *J. Am. Chem. Soc.*, **71**, 2427 (1949).

limed anhydrous ferric chloride and the reaction mixture was maintained between 35° and 55° by immersion in ice. After the reaction mixture had been stirred for an additional 2.5 hours, the iron salts were removed by filtration and the filtrate was fractionated through a 12-inch, helix-packed column to yield 111 g. (45%) of 1,2-diacetoxy-3-butene (XI), b.p. 101-101.5° (24 mm.), n^{23}_{D} 1.4300 [reported[25] b.p. 75–77° (6 mm.), n^{20}_{D} 1.4309].

Pyrolysis of cis-1,4-diacetoxy-2-butene (IX). At the rate of 1 g. per minute, 101 g. (0.59 mole) of *cis*-1,4-diacetoxy-2-butene (IX) was added dropwise to a vertical Vycor tube packed with Pyrex helices and externally heated at 495°, as previously described.[26] The system was continuously flushed with a slow stream of oxygen-free nitrogen to prevent any charring. The pyrolysate, which was collected in a side-arm flask cooled in a Dry Ice-Methyl Cellosolve[27] bath, was dissolved in ether and the solution was washed with a potassium carbonate solution to minimize the loss of the water-soluble products. [Titration of an aliquot of the aqueous washings of a parallel run indicated that 77% of one molar equivalent of acetic acid had been liberated.] After the ether solution had been dried over magnesium sulfate, the ether was removed by distillation and the residue was fractionated and the higher-boiling material was refractionated through a 6-inch, helix-packed column to yield 2.5 g. of a forerun, b.p. 75–77°, n^{25}_{D}1.3800; 17.2 g. (26%) of slightly impure 1-acetoxy-1,3-butadiene (X), b.p. 74° (131 mm.) to 64° (35 mm.), n^{25}_{D} 1.4560; 20.2 g. (20%) of impure 1,2-diacetoxy-3-butene (XI), b.p. 110.5–112° (30–33 mm.), n^{25}_{D} 1.4323, d^{24}_{4} 1.053; and 24.3 g. (24% recovery) of 1,4-diacetoxy-2-butene (IX), b.p. 129–134° (32–33 mm.), n^{25}_{D} 1.4457.

Pyrolysis of 1,2-diacetoxy-3-butene (XI). By the use of the apparatus described above, 84.8 g. (0.492 mole) of 1,2-diacetoxy-3-butene (XI) was pyrolyzed at 495° over a period of 110 minutes. The pyrolysate (72.0 g.) was dissolved in ether and the resulting solution was washed with a potassium carbonate solution. [Titration of an aliquot of the aqueous extracts of a parallel run indicated that 83% of one molar equivalent of acetic acid had been liberated.] After the solution had been dried over magnesium sulfate, the ether was removed by distillation and the residue was fractionated through a 12-inch, helix-packed column to yield 2.1 g. of a forerun, b.p. 24–51° (50 mm.), n^{25}_{D} 1.4253; 16.0 g. (29%) of slightly impure 1-acetoxy-1,3-butadiene (X), b.p. 51–53° (28 mm.), n^{25}_{D} 1.4583; 12.0 g. (14% recovery) of impure 1,2-diacetoxy-3-butene (XI), b.p. 99–107° (20 mm.), n^{25}_{D} 1.4480; and 5 g. (6%) of impure 1,4-diacetoxy-2-butene (IX), b.p. 76–77.5° (1.1 mm.), n^{25}_{D} 1.4537.

Identification of 1-acetoxy-1,3-butadiene (X) *from pyrolyses.* The 1-acetoxy-1,3-butadiene (X) fraction from the pyrolyses possessed a lower refractive index than the authentic sample prepared from crotonaldehyde. In view of the wide variance of refractive indices reported in the literature for X, it did not appear that this diene could be conveniently purified by distillation. For this reason, X was converted to a solid derivative.

A solution of 1.0 g. (0.0089 mole) of 1-acetoxy-1,3-butadiene (X) (from the pyrolysis of either IX or XI), 1.0 g. (0.01 mole) of maleic anhydride, and a trace of *p-tert*-butylcatechol in 10 ml. of dry benzene was heated under reflux for 1.5 hours. The benzene was removed by evaporation and the residue was recrystallized from ether to yield 0.78 g. (42%) of 3-acetoxy-1,2,3,6-tetrahydrophthalic anhydride (XII), m.p. 56.5–58.5° [reported[28] m.p. 58°]. All attempts to isolate the higher-melting 4-acetoxy-1,2,3,6-tetrahydrophthalic anhydride, that would have resulted if any 2-acetoxy-1,3-butadiene had been formed during the pyrolysis of either IX or XI, failed.

Identification of 1,2-diacetoxy-3-butene (XI) *and 1,4-diacetoxy-2-butene* (IX) *from pyrolysis.* The 1,2-diacetoxy-3-butene (XI) and the 1,4-diacetoxy-2-butene (IX) were identified by the comparison of their infrared absorption spectra with those of authentic samples. In general, only the absorption bands in the range 750 to 1360 cm.$^{-1}$ were sufficiently characteristic to be helpful. The bands at 984 and 939 cm.$^{-1}$ were the most characteristic of XI and the band at 965 cm.$^{-1}$ was the most characteristic of IX.

By the use of these three bands the sample of impure 1,2-diacetoxy-3-butene (XI) isolated from the pyrolysis of 1,4-diacetoxy-2-butene (IX) was estimated to consist of 90 to 96% of XI and 3 to 8% of IX. All the high-boiling fractions from the pyrolysis were shown to be essentially mixtures of IX and XI.

The 1,2-diacetoxy-3-butene (XI) recovered from the pyrolysis had a molecular refraction of 42.5 (calculated molecular refraction 42.0).

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[26] Bailey and Golden, *J. Am. Chem. Soc.*, **75**, 4780 (1953).

[27] Trade name for 2-methoxyethanol.

[28] Flaig, *Reichsamt Wirtschaftsausbau, Chem. Ber. Pruf.-Nr.*, **093** (PB 52020), 1073 (1942) [*Chem. Abstr.*, **41**, 6189 (1947)].