

Pyrolysis of Esters. X. Effect of Unsaturation on Direction of Elimination¹WILLIAM J. BAILEY² AND CHARLES KING³

Received March 9, 1956

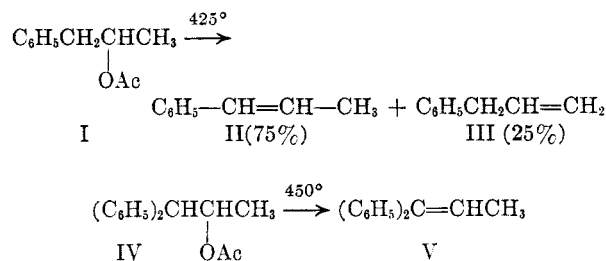
The introduction of unsaturated electron-withdrawing groups in the β -position of the alkyl portion of an ester tends to reverse the direction of elimination during pyrolysis. The acidity of the β -hydrogen appears to be an important factor in determining the direction of elimination. Thus the pyrolysis of β -phenylisopropyl acetate produced a mixture of olefins consisting of 75% 1-phenyl-1-propene and 25% allylbenzene, while the pyrolysis of β,β -diphenylisopropyl acetate gave substantially only 1,1-diphenyl-1-propene. The pyrolysis of ethyl β -acetoxy-*n*-butyrate produced only ethyl crotonate and the pyrolysis of the related ethyl α -methyl- β -acetoxy-*n*-butyrate gave essentially ethyl tiglate.

It was reported recently that the pyrolysis of secondary⁴ and tertiary⁵ esters, in contrast to other elimination reactions, produced essentially a single product, the least highly alkylated olefin, in accordance with the Hofmann rule. The elimination was highly selective with the hydrogen abstracted preferentially from a $\text{CH}_3 > \text{CH}_2 > \text{CH}$. Thus *tert*-amyl acetate gave almost entirely 2-methyl-1-butene⁵ and methylisopropylcarbinyl acetate gave substantially only 3-methyl-1-butene.⁴ This formation of the least highly alkylated olefin not only is a useful tool for the synthesis of otherwise difficultly accessible olefins but also makes possible the isomerization of double bonds from an internal to a terminal position.

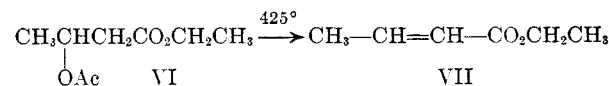
In a research program designed to determine the effect of polar groups on the direction of elimination in the pyrolysis of esters it was found that when an ether group or a tertiary amino group was present the elimination still followed the Hofmann rule. Thus β -methoxyisopropyl acetate produced on pyrolysis methyl allyl ether, while β -dimethylaminoisopropyl acetate gave allyldimethylamine.⁶ Since simple inductive effects do not appear to change the direction of elimination, it was of interest to determine the effect of unsaturation on the direction of elimination in the pyrolysis of esters.

For this reason β -phenylisopropyl acetate (I) was pyrolyzed at 425° under such conditions that only 56% of the theoretical amount of acetic acid was liberated. These relatively mild conditions were chosen to permit maximum selectivity in the elimination and to avoid any carbonization in the pyrolysis tube. It was previously shown^{7,8} that, if carbonization was avoided, no rearrangements oc-

curred during pyrolysis and strained olefins such as 1,2-dimethylene-4-cyclohexene, an isomer of *o*-xylene, could be synthesized in a 92% yield completely free of aromatic compounds. The pyrolysis of I, in contrast to the pyrolysis of simple alkyl esters, did not proceed in a selective manner but produced a mixture of olefins consisting of 75% 1-phenyl-1-propene (II) and 25% allylbenzene (III). Allylbenzene (III) was not isomerized to II under the conditions of the pyrolysis. This influence of the phenyl group is in contrast to the work of Bamberger and Lodter,⁹ who reported that the pyrolysis of 2-acetoxytetralin produced 1,4-dihydronaphthalene.



Since one phenyl group had such a pronounced effect on the direction of elimination, a compound containing two phenyl groups was studied. For this reason β,β -diphenylisopropyl acetate (IV) was pyrolyzed at 450°, under such conditions that 83% of the theoretical amount of acetic acid was eliminated. Only one olefin, 1,1-diphenyl-1-propene (V), was detected from the pyrolysis of IV. The sample of V was assumed to be at least 98% pure because the two possible isomeric products differ considerably in properties.



(1) Previous paper in this series, *J. Org. Chem.*, **21**, 854 (1956).

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

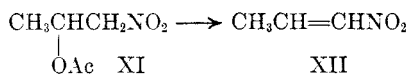
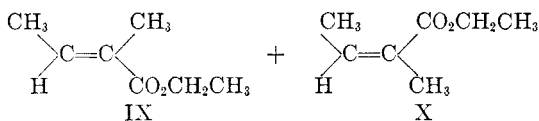
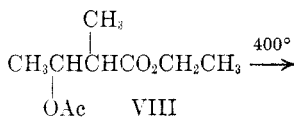
(5) Bailey, Hewitt, and King, *J. Am. Chem. Soc.*, **77**, 357 (1955).

(6) Bailey and Nicholas, *J. Org. Chem.*, **21**, 854 (1956).

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

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

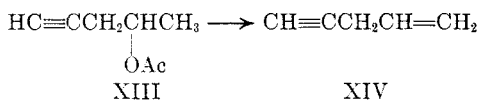
(9) Bamberger and Lodter, *Ber.*, **23**, 209 (1890).



Since a phenyl group is not highly electronegative, a study was made to determine the effect of the unsaturated electron-withdrawing carboxyl group of an ester on the direction of elimination. When ethyl β -acetoxy-*n*-butyrate (VI) was pyrolyzed at 425°, the only product isolated was ethyl crotonate (VII). In an effort to decrease the selectivity of the elimination, a methyl group was introduced in the α -position. However, when ethyl β -acetoxy- α -methylbutyrate (VIII) was pyrolyzed at 400°, again the only product was a mixture of ethyl tiglate (IX) plus a small amount of ethyl angelate (X). No β,γ -unsaturated ester was found. Gold¹⁰ similarly found that the pyrolysis of 2-acetoxy-1-nitropropane (XI) gave 1-nitropropene (XII).

Thus it appears that the highly electron-withdrawing unsaturated groups, such as the carboxyl and nitro, will completely reverse the direction of elimination¹¹ so that the Hofmann rule is no longer followed. When a carboxyl or nitro group is located in the β -position, the identical olefins will be obtained from both the dehydration of the alcohol and the pyrolysis of the corresponding ester.

The phenyl group appears to be intermediate in its influence on the direction of elimination. One β -phenyl group only partially reverses the direction of elimination. Thus, a CH_2 located *alpha* to a phenyl group can successfully compete with a CH_3 to furnish the hydrogen atom for the departing acid. (Dehydration of the corresponding alcohol apparently gives only the olefin with the double bond in

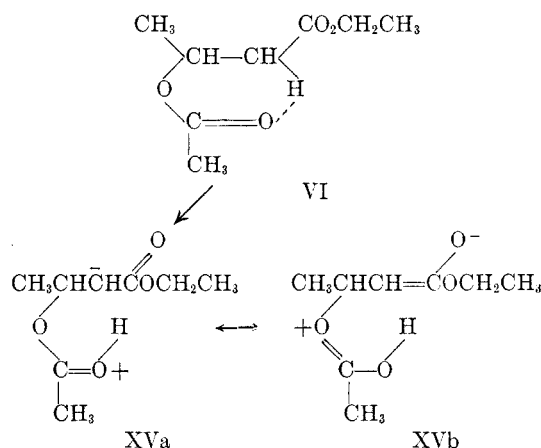


conjugation with the phenyl group.) Only if there are two β -phenyl groups on the same carbon atom, will the influence be strong enough to reverse completely the direction of elimination.

(10) Gold, *J. Am. Chem. Soc.*, **68**, 2544 (1946).

(11) The results are not in complete agreement with the work of Allen and Haury [U.S. Patent 2,225,542 (1940)], who obtained a mixture of 2-penten-4-one and 1-penten-4-one from the pyrolysis of 4-acetoxy-2-pentanone.

Paul and Tchelitcheff¹² found that the pyrolysis of 4-acetoxy-1-pentyne (XIII) at 560° gave a 52% yield of allylacetylene (XIV). It is clear from this example that all unsaturated groups do not reverse the direction of elimination. Thus the stability of the conjugated olefin is not the determining factor. One must conclude that the activation of the hydrogen atom to be abstracted must be very important. Since a methoxyl or a dimethylamino group does not change the direction of elimination, simple inductive effects cannot explain the results. One can postulate that the acidity of the hydrogen atom is increased by the presence of some ionic resonance form in the activated state such as XV.



One would expect that an ester carbonyl or a nitro group would have a large stabilizing effect on such a transient intermediate, while a phenyl group would have an intermediate effect and an acetylene group would have very little stabilizing effect. Resonance with the acetylene group would involve a high energy allene group. Similarly, an ether or an amino group would not be expected to stabilize such a form.

The present work shows that the Hofmann rule for elimination in the pyrolysis of esters is followed by most simple esters but the direction of elimination can be reversed by the presence of an unsaturated electron-withdrawing group in the β -position to the acyloxy group.

EXPERIMENTAL

β -Phenylisopropyl acetate (I). To a solution of 23 g. (0.6 mole) of lithium aluminum hydride in 1000 ml. of anhydrous ether was added dropwise 268 g. (2.0 moles) of 1-phenyl-2-propanone. After the reaction mixture had been stirred for 2 hours, the excess hydride was decomposed with water and the reaction mixture was acidified with 10% hydrochloric acid. The aqueous layer was extracted with ether, and the ether extract was combined with the original organic layer. The ether was removed by distillation and the residue was heated under reflux with 1 liter of acetic anhydride for 12 hours. The reaction mixture was fractionated through an

(12) Paul and Tchelitcheff, *Compt. rend.*, **233**, 1116 (1951).

18-inch, helix-packed column to yield 307 g. (92%) of β -phenylisopropyl acetate (I), b.p. 107–108° (13 mm.), n_D^{20} 1.4876 [reported¹³ (for the optically active form) b.p. 115° (16 mm.), n_D^{20} 1.4897].

Pyrolysis of β -phenylisopropyl acetate (I). At the rate of 1.7 g. per minute, 100 g. (0.60 mole) of β -phenylisopropyl acetate (I) was added dropwise to a vertical Vycor tube packed with 1/8-inch Pyrex helices as described previously.^{7, 14} The pyrolysis tube was externally heated at 425° and continuously flushed with a slow stream of oxygen-free nitrogen. The pyrolysate, which was collected in a side-inlet flask cooled in a Dry Ice-chloroform-carbon tetrachloride bath, was extracted with water to remove the acetic acid and then dried over magnesium sulfate. (Titration of the aqueous extracts with standard base indicated that 56% of the theoretical amount of acetic acid had been liberated.) Fractionation of the hydrocarbon layer through a 12-inch, helix-packed column produced 9.34 g. (13%) of allylbenzene (III), b.p. 155–158° (747 mm.), n_D^{20} 1.5280–1.5290 [reported b.p. 155° (760 mm.),¹⁵ n_D^{20} 1.5200¹⁶] and 28.08 g. (40%) of 1-phenyl-1-propene (II), b.p. 165–168° (747 mm.), n_D^{20} 1.5467–1.5490 [reported b.p. 166.7° (746 mm.),¹⁷ n_D^{20} 1.5493¹⁸].

β,β -Diphenylisopropyl alcohol. To a solution of 7.6 g. (0.20 mole) of lithium aluminum hydride in 500 ml. of ether contained in a 5-liter, three-necked flask equipped with a Hershberg stirrer, a dropping-funnel, and a condenser was added over a period of 20 minutes a solution of 135 g. (0.64 mole) of diphenylacetone,¹⁹ m.p. 60–61°, in 1 liter of ether. After the reaction mixture had been allowed to stand overnight at room temperature, it was heated under reflux for an additional hour. The mixture then was poured slowly onto ice and the suspension was acidified with 1 liter of 5% sulfuric acid. The aqueous layer was extracted with two 200-ml. portions of ether and the extracts were combined with the original ether layer. After the combined ether solutions had been extracted with a saturated sodium bicarbonate solution and then twice with water, the solution was dried over sodium sulfate. The ether was removed by evaporation to produce a residual light-colored viscous oil that solidified on standing. Recrystallization from ligroin produced 135 g. (98%) of β,β -diphenylisopropyl alcohol, m.p. 62–63° (reported²⁰ m.p. 62°). A mixture melting point determination of the alcohol with diphenylacetone showed a depression of 15°.

β,β -Diphenylisopropyl acetate (IV). A mixture of 135 g. (0.63 mole) of β,β -diphenylisopropyl alcohol, 100 g. of acetic anhydride, and 1 ml. of concentrated sulfuric acid was heated under reflux for 12 hours. The reaction mixture was neutralized with a sodium carbonate solution, and the resulting solid was recrystallized from ligroin to yield 86 g. (53%) of β,β -diphenylisopropyl acetate (IV), m.p. 77–78° (reported²⁰ m.p. 77–78°).

Pyrolysis of β,β -diphenylisopropyl acetate (IV). By the use of the apparatus and method described above, 77 g. (0.30 mole) of β,β -diphenylisopropyl acetate (IV) was pyrolyzed

at 450°. Since IV was a solid at room temperature, it was added as a melt to the pyrolysis tube from a dropping-funnel heated with an infrared heat lamp. The pyrolysate was dissolved in ligroin, and the resulting solution was extracted with water to remove the acetic acid. (Titration of the aqueous extracts indicated that 83% of the theoretical amount of acetic acid had been liberated.) After the solution had been dried over magnesium sulfate, the ligroin was removed by evaporation under reduced pressure to yield 45 g. of a light tan solid, m.p. 48–50°, which was recrystallized from 95% ethanol to yield 41.2 g. (71%) of 1,1-diphenyl-1-propene (V), m.p. 50–51° (reported²¹ m.p. 50.0–50.5°). The isomeric 1,1-diphenyl-2-propene is a liquid, b.p. 293°.²⁰

Ethyl β -acetoxy-*n*-butyrate (VI). A mixture of 70 g. (0.57 mole) of ethyl β -hydroxy-*n*-butyrate, b.p. 77–80° (15 mm.), n_D^{20} 1.4188, 45 ml. of acetyl chloride, and 340 ml. of pyridine was heated under reflux for 4 hours and the reaction mixture was worked up in the usual manner. Distillation of the crude ester through a 12-inch, helix-packed column yielded 71 g. (72%) of ethyl β -acetoxy-*n*-butyrate (VI), b.p. 81–83° (6 mm.), n_D^{20} 1.4210 [reported²² b.p. 97.5° (15 mm.)].

Pyrolysis of ethyl β -acetoxy-*n*-butyrate (VI). At a rate of 1.7 g. per minute, 25 g. (0.14 mole) of ethyl β -acetoxy-*n*-butyrate (VI) was dropped through the pyrolysis tube at 425° as described above. The pyrolysate was dissolved in ether and extracted with water to remove the acetic acid. (Titration of an aliquot of the aqueous extracts indicated that 60% of the theoretical amount of acetic acid had been liberated.) The ether solution was dried over potassium carbonate and magnesium sulfate and then was fractionated through a 6-inch, helix-packed column to yield 8.83 g. (56%) of ethyl crotonate (VII), b.p. 138–140° (733 mm.), n_D^{20} 1.4248–1.4250 (reported²³ b.p. 138°, n_D^{20} 1.4252). The reported²⁴ constants for the isomeric ethyl vinylacetate are b.p. 124.0–124.2° (755 mm.), n_D^{20} 1.4105.

A sample of VII was hydrolyzed to obtain crotonic acid, m.p. 71–72° (reported²⁵ m.p. 72°). A mixture melting point determination with an authentic sample showed no depression.

Ethyl α -methyl- β -acetoxy-*n*-butyrate (VIII). Ethyl α -methyl- β -hydroxy-*n*-butyrate was prepared by the method of Blaise²⁶ by reaction of ethyl α -bromopropionate with acetaldehyde in the presence of zinc. A mixture of 126 g. (0.87 mole) of ethyl α -methyl- β -hydroxy-*n*-butyrate, 1000 ml. of acetic anhydride, and 100 ml. of acetic acid was heated under reflux for 24 hours. The reaction mixture was fractionated through a 12-inch, helix-packed column to yield 150 g. (92%) of ethyl α -methyl- β -acetoxy-*n*-butyrate (VIII), b.p. 86–87° (9 mm.), n_D^{20} 1.4182 [reported²⁷ b.p. 97.5° (15 mm.)].

Pyrolysis of ethyl α -methyl- β -acetoxy-*n*-butyrate (VIII). At the rate of 1.3 g. per minute, 100 g. (0.53 mole) of ethyl α -methyl- β -acetoxy-*n*-butyrate (VIII) was dropped through the pyrolysis tube at 400° as described above. The pyrolysate was dissolved in ether and the resulting solution was extracted with water to remove the acetic acid. (Titration of an aliquot of the aqueous extracts indicated that 45% of the theoretical amount of acetic acid had been liberated.) After the ether solution had been dried over potassium carbonate and magnesium sulfate, it was fractionated through a 12-

(13) Kenyon and Pickard, *J. Chem. Soc.*, **105**, 2270 (1914).

(14) Bailey and Hewitt, *J. Org. Chem.*, **21**, 543 (1956).

(15) Hillmer and Schorning, *Z. physik. chem.*, **167A**, 407 (1933).

(16) Egloff, *Physical Constants of Hydrocarbons*, Vol. 3, Reinhold Publishing Corp., New York, 1946, p. 192.

(17) Campbell and O'Connor, *J. Am. Chem. Soc.*, **61**, 2897 (1939).

(18) Stuurman, *Proc. Acad. Sci. Amsterdam*, **38**, 450 (1935).

(19) Schultz and Hickey, *Org. Syntheses*, **29**, 38 (1949).

(20) Levy, Gallais, and Albragam, *Bull. soc. chim.*, **43**, 868 (1928).

(21) von Auwers and Fruhling, *Ann.*, **422**, 196 (1921).

(22) Anschutz and Motschmann, *Ann.*, **392**, 100 (1912).

(23) Heibron, *Dictionary of Organic Compounds*, Vol. 1, Eyre and Spottiswoode, London, 1943, p. 578.

(24) Bruylants, *Bull. soc. chim. Belg.*, **38**, 133 (1929).

(25) Bulk, *Ann.*, **139**, 63 (1866).

(26) Blaise, *Bull. soc. chim.*, [3] **29**, 330 (1903).

(27) Blaise and Herman, *Ann. chim.*, [8] **20**, 190 (1910).

inch, helix-packed column to yield 26 g. (38%) of ethyl tiglate (IX) [plus some ethyl angelate (X)], b.p. 148–150° (742 mm.), n_D^{20} 1.4325–1.4350 [reported²⁸ b.p. 153–156°, n_D^{20} 1.4347]. The reported²⁹ constants for the isomeric ethyl angelate are b.p. 142°, n_D^{20} 1.4304.

A mixture of 2.0 g. of the ethyl tiglate (IX), 10 ml. of

methanol, and 20 ml. of a 40% sodium hydroxide solution was allowed to stand overnight at room temperature and then was evaporated almost to dryness. To the residue were added 10 ml. of water and enough hydrochloric acid to make the solution acidic to Congo Red. The resulting precipitate was removed by filtration and recrystallized from ligroin to yield 0.95 g. of tiglic acid, m.p. 62–64° (reported²⁸ m.p. 62–64°).

(28) Buckles and Mock, *J. Org. Chem.*, **15**, 680 (1950).

(29) von Auwers and Wissebach, *Ber.*, **56**, 724 (1923).

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