TABLE III

Reactants[a]	Temp., °C.	Solvent	% Yield C_6H_5-CO-	% Yield C_6H_5-COOH
VI[b] + NH_3	−33	Ammonia, 25 ml.	70	65
VII + NH_3	−33	Ammonia, 25 ml.	93	86
VII + NH_3	−78	Ammonia, 25 ml.	91	85
VI + C_6H_5-NH_2	25	Ether, 30 ml.	80	70
VI + C_6H_5-NH_2	25	Acetone/H_2O, 20 ml.	81	75
VII + cyclo-C_6H_{11}-NH_2	25	Dimethylaniline, 25 ml.	85	80
VII + CH_3OH	25	Methanol, 25 ml.	92	80
VII + CH_3OH	25	Acetonitrile, 30 ml.	25[c]	21
VII + cyclo-C_6H_{11}-NH_2	25	Acetonitrile, 35 ml.	89	92
VII + C_6H_5-NH_2	25	Acetonitrile, 40 ml.	86	82
VII + C_6H_5-NH_2	25	Dimethylformamide, 40 ml.	86	90

[a] Unless otherwise specified the quantities of reactants used were 0.01 mole. [b] 0.0018 mole of VI used. [c] A large recovery of starting material indicated that this reaction was not completed.

0.61 g. (0.005 mole) of dimethylaniline in 50 ml. of anhydrous ether was added 1.13 g. (0.005 mole) of benzoic anhydride. After standing 1 hr., 10 ml. of 10% hydrochloric acid was added and the ether was evaporated. The heterogenous mixture was treated with chloroform to dissolve the solid. The chloroform was washed with 10% sodium carbonate solution and water. The dried chloroform was evaporated to afford 1.01 g. of benzanilide which was recrystallized from methanol–water to afford 0.70 g. (71%) of material, m.p. 162.2–163.4°. The basic extracts were acidified to yield crude benzoic acid which was recrystallized from hexane to afford 0.90 g. (74%) of benzoic acid, m.p. 121–122°.

The recovered benzoic acid had an activity of 2.02 mμc./mg. C and the benzanilide showed 0.093 mμc./mg. C. These data indicate that 15% of the theoretical amount of C^{14} has been incorporated into the benzanilide.

When benzoic anhydride was allowed to stand under the same conditions but in the absence of aniline, the recovered benzoic anhydride had 0.63 mμc./mg. C which corresponds to 46% equilibration of the C^{14}.

NEW BRUNSWICK, N. J.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE]

Electronic Effects in Elimination Reactions. I. Pyrolysis of Acetates[1]

BY C. H. DEPUY AND R. E. LEARY

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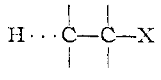
Pyrolytic eliminations of some acetates of substituted 1,3-diphenyl-2-propanols lead to the formation of that olefin which also predominates when the possible olefins are equilibrated and not to the olefin which would be formed by loss of the most acidic hydrogen. It is suggested that in the transition state for acetate pyrolysis reactions, a large amount of double bond character has been developed.

Although the Saytzeff and Hofmann rules—which allow the position of the double bond in unsymmetrical elimination reactions to be predicted—have been formulated for nearly a century, the underlying steric and electronic effects which determine this position still are not fully understood. The most generally accepted interpretation of the rules is that of Hughes and Ingold.[2] According to their view, in the Hofmann elimination (elimination from trialkylammonium or dialkylsulfonium salts with base) the most acidic hydrogen is removed and the direction of elimination is determined by this factor. In the Saytzeff elimination (elimination of halogen or other neutral anions), the stability of the resulting olefinic product is the more important factor and controls the direction of elimination. Hyperconjugative factors were postulated to be of primary importance. Recently Brown and co-workers[3] have demonstrated the importance of steric effects in directing eliminations.

A priori, an elimination of the type I might be imagined to have a whole spectrum of transition

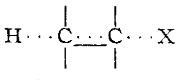
$$\text{H-C-C-X} \longrightarrow \text{H}^+ \text{ C=C X}^- \qquad \text{(I)}$$

states available to it, depending upon the nature of the group X, the particular mechanism of the elimination, the type of solvent and a host of other factors. As one extreme, a case might be imagined in which the carbon–hydrogen bond is completely broken before the C–X bond has even started to rupture, II. At the other extreme, both the C–H



$$\text{H}\cdots\text{C—C—X} \qquad \text{(II)}$$

and C–X bonds might be very much broken in the transition state, III. Other situations may be imagined. An understanding of the structural



$$\text{H}\cdots\text{C}\cdots\text{C}\cdots\text{X} \qquad \text{(III)}$$

factors that affect the transition state configuration could allow more control over the nature of the product to be expected in eliminations and the amount of olefin being formed in competing reac-

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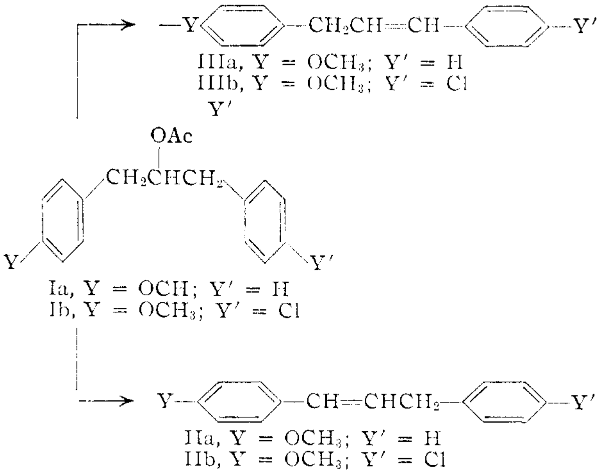
[1] This work was supported by a grant from the Research Corporation.

[2] For a general discussion of elimination reactions and for the conclusions of Ingold and co-workers about the Hofmann and Saytzeff rules, see C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, pp. 420–472.

[3] H. C. Brown and I. Moritani, THIS JOURNAL, **78**, 2203 (1956), and preceding papers.

tions. To this end we have begun a general investigation of the effect of various electronic factors on the rate of several elimination reactions.

In studying elimination reactions, we wished to choose a system in which we could readily determine both the acidity of the hydrogens being removed and the relative stability of the olefins being formed. In addition, we desired a system in which base-catalyzed eliminations could be followed kinetically, and at the same time eliminations could be studied in which kinetic data would be either difficult to obtain (pyrolytic eliminations) or of no value (first-order eliminations). For this investigation we have chosen compounds of the type I. These 1,3-diphenyl-2-propyl compounds offered the possibility of studying relative rates of eliminations where actual rate measurements were not possible. Thus, in a pyrolytic elimination of acetic acid the rate for a substituted benzene ring could be compared to the rate for an unsubstituted ring by analyzing the olefin mixture for the relative amounts of olefins II and III. Variations in the nature of the substituent would allow a Hammett $\sigma-\rho$ treatment to be carried out. Concurrently a straight kinetic investigation of base-catalyzed eliminations in the simpler but analogous β-phenyl ethyl system was begun.



IIIa, Y = OCH_3; Y' = H
IIIb, Y = OCH_3; Y' = Cl

Ia, Y = OCH; Y' = H
Ib, Y = OCH_3; Y' = Cl

IIa, Y = OCH_3; Y' = H
IIb, Y = OCH_3; Y' = Cl

If the system I appeared satisfactory from the standpoint of kinetics, it also seemed attractive for the investigation of both the stabilities of the resulttant olefins and the acidities of the hydrogens. Thus, Ingold and Shoppee[4] had shown that olefins of this type could be equilibrated in base and, of course, the proportion at equilibrium would reflect the relative thermodynamic stabilities of the two olefins. The relative hydrogen acidities could be estimated from the Hammett σ-values of the substituent groups and, if more precise data were deemed necessary, a study of the *rates* of the equilibration of the olefins would be indicative. Two other advantages of this system made its selection propitious. First the absence of selective steric effects served to simplify the interpretation of results, and secondly the ease of analysis of the mixture of products, as will be discussed below, offered the possibility of studying a number of different eliminations with the same system.

Synthesis.—For reasons that will become apparent in the discussion of the analytical method, it was felt desirable to have Y = OCH_3. In order to make the rate differences as large as possible, the presence of a *p*-chloro group seemed desirable. In base-induced eliminations where hydrogen acidity is important, the presence of a *p*-chloro group favors the elimination by a factor of nearly ten.[5] On the other hand, a *p*-methoxyl group conjugates well with a double bond[3] and would be expected to accelerate those reactions in which the relative stability of the olefin played a dominant role. For this reason Ia and Ib were synthesized. The synthesis of the requisite alcohols are summarized in Charts I and II. These paths had the advantage over other imaginable paths of providing the olefins for equilibration and analysis studies.

Analytical Method.—In the pyrolysis of the acetates the two possible olefins would be obtained together with varying amounts of unreacted acetate. Other contaminants were to be anticipated when these compounds were applied to the study of other elimination reactions. While spectral analysis would probably be possible in this system, it appeared to be extremely difficult to make general. In choosing these particular compounds for the study, we planned to make use of the well-known variation in the reactivity of substituted benzyl compounds.[6] The mixture of olefins was converted to a mixture of benzyl bromides with HBr in methylene chloride under conditions where the initial acetate was unreactive. These solutions were made up to a known volume with absolute acetone and, after the addition of a small amount of water, the bromides allowed to solvolyze. The *p*-methoxybenzyl bromides formed by addition of HBr to olefins IIa and IIb solvolyzed very rapidly as compared to either the unsubstituted (from IIb) or *p*-chloro bromides (from IIc), and titration of the liberated acid after about 40 minutes at 25° gave the amount of this bromide present. Solvolysis at higher temperatures with more water added, or reaction with silver nitrate solution, was used to get the total halide and from this the amount of unsubstituted or *p*-chlorobenzyl bromide. By this method known mixtures could be determined to within 3%. It should be pointed out that the large differences in solvolysis rate which were utilized in these experiments are not necessary for the analytical method to be useful. Differences of a factor of three or less are sufficient if more kinetic points are taken.

Results and Discussion

Acetate pyrolysis reactions have been extensively investigated by Bailey and co-workers[7] in an effort to determine the direction of elimination. In three aliphatic cases the Hofmann rule was obeyed exclusively, that is, the hydrogen was abstracted from a CH_3 group in preference to a CH_2 group and from a CH_2 group in preference to a C–H group. This preference for the methyl hydrogen

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(4) C. K. Ingold and C. W. Shoppee, *J. Chem. Soc.*, 447 (1929).

(5) C. H. DePuy and D. H. Froemsdorf, This Journal, **79**, 3710 (1957).

(6) J. K. Kochi and G. S. Hammond, *ibid.*, **75**, 3445 (1953).

(7) W. J. Bailey and C. King, *ibid.*, **77**, 75 (1955); W. J. Bailey and L. Nicholas, *J. Org. Chem.*, **21**, 854 (1956).

CHART I

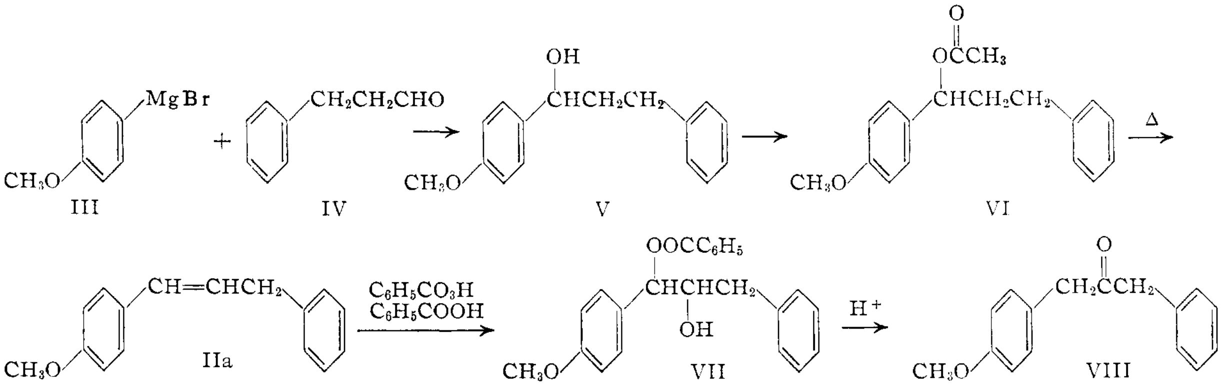
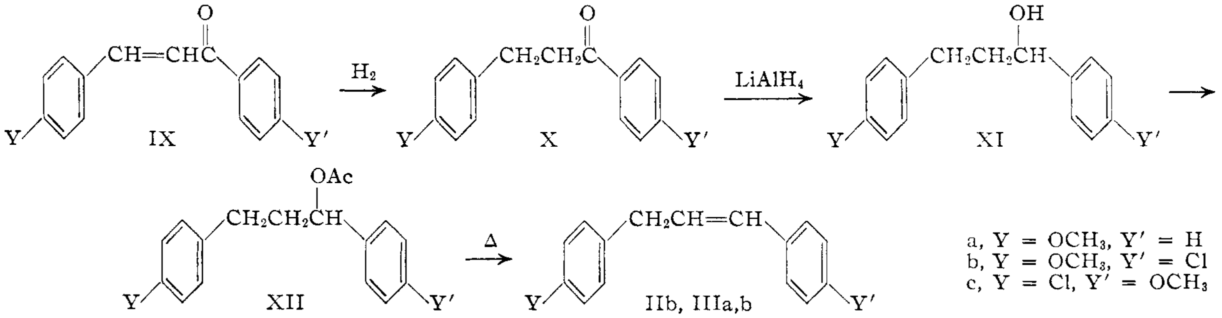


CHART II



a, Y = OCH_3, Y′ = H
b, Y = OCH_3, Y′ = Cl
c, Y = Cl, Y′ = OCH_3

was observed again in the pyrolysis[8] of 1-methoxy-2-propyl acetate and in 1-dimethylamino-2-propyl acetate. However, in compounds containing a benzene ring, Hofmann control was less complete. In 1-phenyl-1-propyl acetate, 75% of the resultant olefin was conjugated to the benzene ring; and this rose to 100% in the case of 1,1-diphenyl-2-propyl acetate.[9] Compounds containing nitro[10] and ester[9] groups also have given products not in accordance with the Hofmann rule.[11] In these cases the olefin formed was found to be conjugated with the unsaturated group. Bailey has interpreted these results to mean that the acidity of the hydrogen being removed is primarily responsible for determining the direction of elimination. Since our system gave a means of checking this conclusion where the various electronic influences were determinable and since, in addition, steric factors were the same for the competing eliminations, we decided to investigate the electronic effects in acetate pyrolyses as the first case in our general study of elimination reactions.

From the standpoint of its electronic effects, a *p*-methoxyl group appeared to be a desirable substituent. From its σ-value (-0.268)[12] it could be predicted to have the effect of decreasing the acidity of the benzyl hydrogens and so of making eliminations slower which depended on this acidity.[5] Ingold and Shoppee[4] have measured the position of equilibrium of the olefins IIa and IIIa and had found that IIa, in which the olefin was conjugated to the methoxyl group, predominated at equilibrium by a factor of 2.3. As a consequence, olefin IIa is the more stable of the two and should predominate in the pyrolysis if olefin stability is the more important effect in the transition state.

The results of a number of pyrolyses of acetate Ia under different conditions are summarized in Table I. Under all conditions investigated, the more thermodynamically stable of the two possible olefins is formed in the elimination. In fact, the olefin proportion is the same, within experimental error, as that which would result from equilibration.

TABLE I

PYROLYSIS OF 1-PHENYL-3-*p*-METHOXYPHENYL-2-PROPYL ACETATE

Phase	Conversion, %	*p*-Methoxy (IIa), %	Hydrogen (IIIa), %
Liquid	47	70	30
Vapor	46	75	25
Vapor	20	73	27
Vapor	. .	70	30
Liquid	11	75	25

We next investigated a compound in which the difference in hydrogen acidity would be even larger than was the case in Ia. Replacement of the *p*-hydrogen with a chlorine ($\sigma = +0.227$) gave Ib in which the benzyl hydrogen acidity was greatly enhanced. On the other hand, our equilibration experiments showed that at equilibrium the *p*-methoxyl olefin should still predominate. The results of these pyrolyses, summarized in Table II, again indicate that the stability of the olefin being formed is controlling the direction of the elimination.

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(8) W. J. Bailey and L. Nicholas, *J. Org. Chem.*, **21**, 648 (1952).

(9) W. J. Bailey and C. King, *ibid.*, **21**, 858 (1956).

(10) M. H. Gold, *ibid.*, **68**, 2544 (1946).

(11) Bailey[8] appears to have misconstrued the results of Paul and Tchelitcheff, *Compt. rend.*, **233**, 1116 (1951), on the pyrolysis of an acetylenic acetate.

(12) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, Chapt. VII.

Table II

Pyrolysis of 1-(*p*-Chlorophenyl)-3-(*p*-methoxyphenyl)-2-propyl Acetate

Phase	Conversion, %	*p*-Methoxy (IIb), %	*p*-Chloro (IIIb), %
Liquid	13	84	16
Vapor	20	87	13
Vapor	26	77	23
Vapor	46	87	13

Because of the fact that the pyrolysis products and the equilibrium products were the same, it had to be demonstrated that the actual products isolated were those arising directly from the elimination and not being formed by equilibration of an initially formed mixture of a different composition. To establish that the products are stable to the reaction conditions, we have carried out the following experiments. (1) Pure olefins were subjected to the conditions of the reactions and did not equilibrate. (2) Benzyl acetate XIIa on vapor phase pyrolysis gave only IIIa, uncontaminated with its isomer, despite the fact that the isomer formed is the least stable of the pair and that small quantities of the other isomer would be easily detectable by our analytical method. (3) Liquid phase eliminations of the four possible benzyl acetates in the synthetic procedures, followed by distillation, gave high yields (about 70%) of the corresponding olefins which were uncontaminated with the other isomer. We believe that these control experiments establish the absence of post-equilibration to a high degree of probability.

Our results demonstrate that the relative stabilities of the olefins being formed are instrumental in determining the rate of eliminations and that, at least in our system, relative hydrogen acidity is not of importance. In compounds with very acidic hydrogens, as in the nitro and carbethoxy cases, it may be that resonance stabilization of anions is important; but our data make it unlikely that hydrogen acidity is important in the simple aliphatic systems. It seems more probable that steric factors are playing an important role in determining the course of the reaction[13] in these cases and that only when steric factors are canceled out, or the electronic effects become overpowering, do non-Hofmann products arise.

A transition state whose structure is rather close to that of the olefin seems a reasonable one for the acetate pyrolysis. Both the leaving group ($-OOCCH_3$) and the base (O═C) are weak, and simultaneous breaking of both the C–H and C–O bonds would be expected. The elimination would be anticipated to be much less exothermic than the E_2 reaction of the corresponding halides, and hence the transition state would occur well along the reaction coördinates.[14] This would lead to appreciable double bond character in the carbon–carbon bond, and interactions between this developing double bond and the aromatic substituents would parallel the interaction found in the olefinic products.

An alternative mechanism for these pyrolytic eliminations appeared possible. In this mechanism the C–O bond-breaking would precede C–H bond-breaking, and the elimination would be in reality an E_1 type. Since E_1 eliminations have been assumed to give the most stable olefin as product, this would be in accord with the facts. To rule out this possibility, we ran liquid phase eliminations of the *p*-methoxybenzyl acetate VI and the unsubstituted benzyl acetate XIIa. If the elimination were E_1 in character, the *p*-methoxyl acetate would be expected to eliminate many times faster than the unsubstituted acetate. However, the actual differences in rate were small and consistent with the view that differences in stability of the olefins being formed in the two cases were responsible for the differences in rates.

It seems probable then that the transition state for ester pyrolysis reactions is well along toward products and that, in the absence of steric effects, the olefin stability, as reflected in the transition state, determines the direction which the elimination will take. Strongly acid-strengthening groups may affect the timing of the C–H and C–O bond-breaking steps enough to exert a specific control on the reaction.

Experimental[15]

Preparation of 1-(*p*-Anisyl)-3-phenylpropanol (V).—To a Grignard reagent prepared from 9 g. (0.375 mole) of Mg and 70 g. (0.375 mole) of *p*-bromoanisole in 250 ml. of ether was added slowly a solution of 44 g. (0.328 mole) of freshly distilled hydrocinnamaldehyde in ether. After the addition was complete, the mixture was heated at reflux for 0.5 hr. and decomposed by the addition of 450 ml. of a cold, saturated solution of ammonium chloride. After washing and drying, the ether was removed and the oily residue distilled. The product (56.5 g., 71% yield, b.p. 175–180° (0.5 mm.)) crystallized upon scratching. Recrystallization from hexane gave needles, m.p. 46–48°. Several times during distillations, spontaneous elimination occurred giving the olefin IIa directly.

Preparation of 1-(*p*-Anisyl)-3-phenylpropene (IIa).—The olefins could best be prepared in a pure form by liquid phase pyrolysis of the acetates. The alcohol V was acetylated with pyridine and acetic anhydride to give **1-(*p*-anisyl)-3-phenylpropyl acetate (VI)**, b.p. 170–175° (1 mm.), $n^{18}D$ 1.5458. The acetate (10 g.) was placed in a small distilling flask equipped with a short column and a graduated centrifuge tube as a receiver. The liquid was heated with a soft bunsen flame until acetic acid began to distil. Heating was continued at such a rate that the acetic acid distilled rapidly and until the calculated amount had been collected. The residue was then cooled, taken up in methylene chloride and washed free of any excess acid. Distillation gave 5.5 g. (70% yield) of olefin, b.p. 160° (1 mm.).

Anal. Calcd. for $C_{16}H_{16}O$: C, 85.68; H, 7.19. Found: C, 85.80; H, 7.04.

Preparation of Hydroxybenzoate VII.—A cold mixture of the olefin IIa (45 g., 0.2 mole) and 24 g. (0.2 mole) of benzoic acid in 240 ml. of methylene chloride was added over 0.5 hr. to a cold solution of 30 g. (0.23 mole) of perbenzoic acid in methylene chloride. The solution was stirred and kept below 5° with an ice-bath during the addition. After the solution stood overnight at 4°, the excess acid was removed by extraction and the methylene chloride removed. The crystalline hydroxybenzoate which remained could be used in the next step without further purification. A sample crystallized from aqueous alcohol gave m.p. 98–99°.

Anal. Calcd. for $C_{23}H_{22}O_4$: C, 76.22; H, 6.12. Found: C, 75.94; H, 6.06.

Preparation of 1-(*p*-Anisyl)-3-phenylpropanol-2 (Ia).—A solution of 40 ml. of concd. H_2SO_4, 40 ml. of water and 250 ml. of alcohol was added to 40 g. of the hydroxybenzoate

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(13) But see T. D. Nevitt and G. S. Hammond, **This Journal**, **76**, 4124 (1954), for an all-aliphatic case where product stability may be important.

(14) G. S. Hammond, *ibid.*, **77**, 334 (1955).

(15) The use of the Baird infrared spectrophotometer of the Institute of Atomic Research, Ames, Iowa, is hereby gratefully acknowledged.

and the mixture heated at reflux for 3.5 hr. After cooling the mixture, water (200 ml.) was added and the ketone extracted with three 150-ml. portions of ether. The extracts were washed with carbonate and water and the solution dried. Distillation gave the ketone (b.p. 160–170° (1 mm.)) which could not be induced to crystallize. The crude ketone was reduced with lithium aluminum hydride to give, after distillation at 175–180° (1.5 mm.), a colorless oil which soon crystallized. Recrystallization from pentane and then from alcohol gave Ia as long needles; yield 20 g., 71% (based on hydroxybenzoate), m.p. 48–48.5°. Admixtures with alcohols V and XIa showed large depressions in melting points.

Anal. Calcd. for $C_{16}H_{18}O_2$: C, 79.68; H, 7.49. Found: C, 79.50; H, 7.50.

The acetate, prepared in the usual manner, had b.p. 188–190° (0.5 mm.). *Anal.* Calcd. for $C_{18}H_{20}O_3$: C, 76.03; H, 7.09. Found: C, 76.10; H, 7.18.

Preparation of 1-Phenyl-3-(*p*-anisyl)-1-propene (IIIa).—*p*-Anisaldehyde and acetophenone were condensed and reduced catalytically according to the method of reference 16 to give 1-phenyl-3-(*p*-anisyl)-1-propanone (Xa), m.p. 65–66°. Lithium aluminum hydride reduction gave the alcohol XIa, m.p. 64–65°.

Anal. Calcd. for $C_{16}H_{18}O_2$: C, 79.68; H, 7.49. Found: C, 78.95; H, 7.20.

Acetylation gave the acetate, b.p. 166–170° (0.7 mm.).

Anal. Calcd. for $C_{18}H_{20}O_3$: C, 76.03; H, 7.09. Found: C, 76.20; H, 6.95.

Pyrolysis of the ester by heating 30 g. in a pear flask with a free flame until approximately the calculated amount of acetic acid distilled and distillation of the residue gave the olefin, b.p. 147–148° (0.3 mm.), $n^{24}D$ 1.5948.

Anal. Calcd. for $C_{16}H_{16}O$: C, 85.68; H, 7.19. Found: C, 85.90; H, 7.20.

Addition of HBr in methylene chloride to a sample of this olefin and subsequent solvolysis showed it to be uncontaminated with the other isomer.

Preparation of 1-(*p*-Anisyl)-3-(*p*-chlorophenyl)-1-propanol (XIc).—This alcohol, prepared by $LiAlH_4$ reduction of the corresponding ketone Xc,[15] was distilled at 196–200° (1 mm.). It could not be induced to crystallize.

Preparation of 1-(*p*-Anisyl)-3-(*p*-chlorophenyl)-2-propanol.—This alcohol was synthesized using the same procedure as above. In this series the hydroxybenzoate failed to crystallize, but the oily product was used directly to furnish crystalline ketone, m.p. 42–44°. Lithium aluminum hydride reduction of this ketone gave the alcohol, m.p. 69–69.5° after recrystallization first from hexane and then from alcohol–water.

Anal. Calcd. for $C_{16}H_{17}O_2Cl$: C, 69.43; H, 6.19; Cl, 12.85. Found: C, 69.60; H, 6.43; Cl, 12.70.

The acetate, prepared in the usual manner, had m.p. 64–65°. *Anal.* Calcd. for $C_{18}H_{19}O_3Cl$: C, 67.81; H, 6.01; Cl, 11.12. Found: C, 68.09; H, 6.09; Cl, 11.15.

Pyrolysis.—The pyrolyses were carried out by two different methods. In the liquid phase experiments the pure liquid acetates, together with a crystal of a polymerization inhibitor, were heated in a small flask until approximately 50% of the calculated amount of acetic acid was collected. The residue was taken up in ether or methylene chloride and washed free of acetic acid. The solvent was then removed and the residue analyzed. In the vapor phase experiments pure liquid acetate was added dropwise to the top of a vertical glass pyrolysis tube, electrically heated and equipped with a thermocouple. The tube was heated to 500°. Glass beads and glass helices gave identical results when used as packing for the tube. To minimize carbonization, eliminations were carried out to 20–50% conversion. The products were collected in a Dry Ice trap, an aliquot was removed and analyzed for acetic acid and the remainder was washed free of acid, dried and the solvent was removed. Samples of the residue were analyzed for the olefin proportions and other samples for unreacted acetate and total olefin.

Analytical Methods.—In a typical experiment 1.0746 g. of the pyrolysis mixture of Ia was dissolved in 5 ml. of purified CH_2Cl_2. The solution, in a centrifuge tube equipped with a gas inlet tube, was cooled to −10° and gaseous HBr, from a sample collected in Dry Ice, was passed in. When an excess had been added, fumes of HBr began to appear and the addition was stopped. After an additional minute to ensure completion of the reaction, N_2 gas was passed through the solution to remove as much of the excess HBr as possible. The solution was transferred to a 50-ml. volumetric flask and diluted to 50 ml. with anhydrous acetone. A 5-ml. aliquot was removed and the excess HBr was determined by titration with triethylamine in acetone. The sample required 0.09 ml. of 0.1 *N* base. Water (2 ml.) was added and the flask was placed in a constant temperature bath at 25°; 5-ml. samples were removed periodically and titrated. After 40 minutes, 1.80 ml. of amine was required, and this amount did not change after an additional 30 minutes at this temperature. This corresponds to 0.160 meq. of bromide conjugated to the *p*-anisyl group. Another 5-ml. sample of the solution was added to 5 ml. of standard aqueous silver nitrate solution, and the excess silver was determined by titration with standard thiocyanate. Silver (0.213 meq.) was used. Therefore, the olefin was 75% IIa and 25% IIIa. The sample contained 46% olefin. Titration of the acetic acid liberated in the pyrolysis had indicated that 47% reaction had taken place. A saponification equivalent on a sample of the pyrolysis product showed it to contain 51% unreacted acetate. Hence, 97–98% of the product was accounted for. At higher conversions the percentage of the product which could be accounted for by this method dropped off, presumably because of polymerization of the olefinic products, and olefin proportions from these runs are not reported.

Equilibration of Olefins.—The procedure was that of Ingold and Shoppee[4] except that the olefins were analyzed by the reaction with HBr described above. In the case of the IIa–IIIa equilibrium Ingold and Shoppee reported a 70–30 mixture and our results confirmed this. In the case of IIb–IIIb we found 85% IIb and 15% IIIb.

Control Experiments.—1-Phenyl-3-(*p*-anisyl)-1-propyl acetate (XIIa) was pyrolyzed over both glass beads and glass helices at 550°. The product was analyzed in the usual manner. In three runs with conversions up to 42% no easily solvolyzable bromide could be detected and the olefin was completely non-equilibrated. Samples of the pure olefins were passed through the pyrolysis tube and subsequently analyzed for olefin proportion. They were free of detectable amounts of the other isomer. Olefins prepared in the synthetic scheme by liquid phase pyrolysis were analyzed and shown to be uncontaminated with the isomers.

A sample of the pure 2-propylacetates Ia and Ib were subjected to the conditions of the analytical procedure. No detectable solvolyzable bromide was formed, nor was any silver bromide precipitated. In the cases of the benzyl acetates, XII, HBr was absorbed to form presumably the benzyl bromides.

Solvents and Reagents.—The acetone was purified by refluxing with potassium permanganate and drying with Drierite. It was then distilled through a 50-plate column. The triethylamine was refluxed over sodium for 0.5 hr. and then distilled through a 50-plate column; b.p. 88.0°. The indicator was a mixture of brom cresol green and methyl red.[5]

Competitive Pyrolyses of Benzyl Acetates.—Two grams of 1-(*p*-anisyl)-3-phenyl-1-propyl acetate (V), and 1-phenyl-3-(*p*-anisyl)-1-propyl acetate (XIIa), were placed in separate test-tubes and simultaneously placed in a Woods metal-bath at 320° for three minutes. The samples were removed at the same time and analyzed for olefin by reaction in methylene chloride solution with a standard solution of perbenzoic acid. Under these conditions V developed 74% olefin and XIIIa developed 20%.

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(16) "Organic Syntheses," Coll. Vol. I, John Wiley & Sons, Inc., New York, N. Y., 1941, p. 101.