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Pyrolytic *cis* Eliminations: the Pyrolysis of *sec*-Butyl Derivatives¹By C. H. DEPUY, C. A. BISHOP AND C. N. GOEDERS²

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In an attempt to compare the electronic and steric demands of a variety of pyrolytic *cis* eliminations, *sec*-butyl acetate, benzoate, formate, pivalate, methyl carbonate, mono- and dichloroacetate, trifluoroacetate, xanthate, acetamide and vinyl ether have been pyrolyzed and the relative amounts of 1-butene, *cis*- and *trans*-2-butene produced were measured. All esters gave nearly the same product distribution, but the other groups gave substantially greater amounts of 2-olefins. Similar results were obtained in the pyrolysis of selected *t*-amyl and 2-octyl derivatives. Some relative rates of pyrolysis are reported as well as product distribution in the pyrolysis of a number of 2-*n*-alkyl acetates.

A number of organic compounds including esters, xanthates, amine oxides, vinyl ethers and amides undergo pyrolysis with the formation of olefins.³ Acetates⁴ and amine oxides⁵ have been studied recently in attempts to elucidate the factors which determine the direction of elimination, but almost no information is available about directional effects with other leaving groups. In general, in the few systems where direct comparisons have been made, amides^{6,7} and xanthates³ have been reported to furnish, on pyrolysis, olefin mixtures nearly identical in composition with those formed on pyrolysis of the corresponding acetate. Nevertheless, it seemed surprising that reactions proceeding at temperatures which varied by as much as 400° and which involved different atoms in the reaction cycle should give identical product mixtures. We therefore examined the products from the pyrolysis of a variety of *sec*-butyl compounds in order to compare the amounts of 1-butene, *cis*-2-butene and *trans*-2-butene formed.

We first examined the effect on the product distribution of increasing the strength of the acidic portion being eliminated. The haloacetates seemed especially useful in this respect, for a reasonably graded series of *pK*'s could be obtained. The results of these pyrolyses are given in Table I. These pyrolyses were complicated by the observation that the acidic products were not all completely stable to the reaction conditions and the olefinic products were isomerized by the acids formed. The trichloroacetate of *sec*-butyl alcohol could not be studied at all because of the large amounts of hydrochloric acid formed in its pyrolysis. The addition of approximately equal amounts of pyridine and/or toluene to the esters before pyrolysis served as a trap or diluent for these acidic products and led to reproducible results.

A variety of other esters has at one time or another been pyrolyzed and might be expected to lead to somewhat different product distributions from the acetates. The results of pyrolysis of four of these are recorded in Table II. Other deriva-

TABLE I
EFFECT OF ACID STRENGTH ON THE PRODUCT DISTRIBUTION IN THE PYROLYSIS OF *sec*-BUTYL ESTERS

Ester	Temp., °C.	Additive	1-Butene	2-Butene <i>trans</i>	2-Butene <i>cis</i>
Acetate	450	None	57	28	15
Monochloroacetate	375	None	57	28	15
Dichloroacetate	350	None	52	30	18
	340	Pyridine	55	30	15
	425	Toluene	54	30	16
	425	Pyr. + toluene	56	29	16
Trifluoroacetate	350	None	40-52	31-34	17-26
	335	Pyr. + toluene	52	31	17

tives of alcohols also lead, on pyrolysis, to olefins. In Table III are listed the olefin distributions in the pyrolysis of a number of these, together with literature values for the olefin distributions produced on pyrolysis of some acetates and amine oxides.

TABLE II
PRODUCT DISTRIBUTION IN THE PYROLYSIS OF SOME *sec*-BUTYL ESTERS

Ester	Temp., °C.	Additives	1-Butene	2-Butene <i>trans</i>	2-Butene <i>cis</i>
Benzoate	400	None	52	30	18
Formate	450	None	51	31	18
	450	Toluene	51	31	18
Pivalate	460	None	57	28	15
Methyl carbonate	450	None	57	28	15

Table IV reports the relative rates of pyrolysis of some representative *sec*-butyl derivatives. Finally, Table V gives the olefin distributions in the pyrolysis of a number of secondary alkyl acetates.

Discussion

When *sec*-butyl acetate is pyrolyzed a mixture of olefins is formed in nearly quantitative yield. This mixture contains 57% 1-butene, 28% *trans*-2-butene and 15% *cis*-2-butene.⁴ The composition of this mixture is practically independent of reaction conditions and is extremely reproducible. The amounts of the various olefins formed can be rationalized in terms of steric, thermodynamic and statistical effects. An interpretation of the mechanism of the ester pyrolysis reaction in terms of a highly concerted transition state with little charge separation has been put forth.³ This picture is to be contrasted with that drawn for the pyrolytic elimination reaction of alkyl halides, in which heterolytic carbon-halogen bond breaking is suggested to play an important role and a con-

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(2) N.S.F. Summer Research Participation Fellow, 1959.

(3) For a comprehensive discussion see C. H. DePuy and R. W. King, *Chem. Revs.*, **60**, 431 (1960).

(4) D. H. Froemsdorf, C. H. Collins, G. S. Hammond and C. H. DePuy, *J. Am. Chem. Soc.*, **81**, 643 (1959).

(5) A. C. Cope, N. A. LeBel, N. H. Lee and W. R. Moore, *ibid.*, **79**, 4720 (1957).

(6) W. J. Bailey and W. F. Hale, *ibid.*, **81**, 651 (1959).

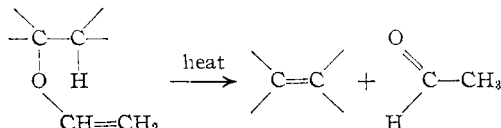
(7) H. E. Baumgarten, F. A. Bower, R. A. Setterquist and R. E. Allen, *ibid.*, **80**, 4588 (1958).

siderable amount of charge separation appears to take place in the transition state.⁸

The products from the pyrolysis of *sec*-butyl halides consist mainly of 2-butene.^{8,9} Esters substituted with electron-withdrawing groups undergo pyrolysis at lower temperatures as compared to acetates. It seemed possible that these esters of stronger acids could undergo elimination by successively more polar mechanisms, leading possibly to a gradual increase in the proportions of 2-butene. The results given in Table I show that this is not the case. Only with *sec*-butyl trifluoroacetate is the amount of 2-butene appreciably increased. This increase is probably real, although it is difficult to prevent isomerization of the olefins by the acids formed. Nevertheless, the change in the amount of 2-butene formed is very small over the series and shows again that the ester pyrolysis reaction is not sensitive to inductive or resonance effects. These results also weaken somewhat, in our opinion, the argument that the greater amounts of 2-butene formed in halide pyrolyses is evidence for a polar transition state in that reaction. It may simply be that the much smaller ring size in the latter elimination leads to the observed results.

Several other esters of *sec*-butyl alcohol were pyrolyzed and the olefin distributions determined, as recorded in Table II. The pyrolysis of the pivalate shows that steric effects in the ester have no effect on the direction of elimination. The slightly greater amounts of 2-butenes from pyrolysis of the formate and benzoate have no obvious explanation at present.

We next turned our attention to the olefin distribution in the pyrolysis of a variety of other derivatives of alcohols. Vinyl ethers have been shown to form, on pyrolysis, olefin and acetaldehyde. For several primary ethers the reaction has



been studied kinetically.¹⁰⁻¹² The elimination takes place at nearly the same rate as that of the corresponding formate, but no studies have been made on the direction of elimination. *sec*-Butyl vinyl ether was prepared by the method of Watanabe.¹³ Pyrolysis at 450° gave 47% 1-butene, 37% *trans*-2-butene and 16% *cis*-2-butene. The proportionately larger amount of internal olefin formed in the pyrolysis of vinyl ethers than in the corresponding acetate is shown also with *t*-amyl vinyl ether. Table III shows that the esters give rise to the largest amounts of 1-olefin, with amide and vinyl ethers next and xanthates the least.

(8) For a summary with much unpublished work see A. Maccoll in "Theoretical Organic Chemistry," Papers presented to the Kekulé Symposium, London, 1958, Butterworth, London, 1959, p. 230.

(9) The amount is reported to vary from 60% 2-butene from *sec*-butyl chloride to 80% from *sec*-butyl iodide. Equilibration of *cis*- and *trans*-olefin occurred during the course of the reaction.

(10) F. W. Schuler and G. W. Murphy, *J. Am. Chem. Soc.*, **72**, 3155 (1950).

(11) A. T. Blades and G. W. Murphy, *ibid.*, **74**, 1039 (1952).

(12) L. Stein and G. W. Murphy, *ibid.*, **74**, 1041 (1952).

(13) W. H. Watanabe and L. E. Conlon, *ibid.*, **79**, 2828 (1957).

It has often been noted that esters of carboxylic acids stronger than acetic acid undergo pyrolysis at lower temperatures than acetates.^{14,15} It has not been determined in any quantitative way just how much the rate of pyrolysis is increased. We have determined some relative rates of pyrolysis

TABLE III

RELATIVE PERCENTAGES OF OLEFINS FORMED IN PYROLYSIS OF VINYL ETHERS, ACETAMIDES AND XANTHATES^a

Compound	Pyrolysis temp., °C.	1-Olefin	2-Olefin	
			<i>trans</i>	<i>cis</i>
<i>sec</i> -Butyl acetate	450	57	28	15
<i>sec</i> -Butyl xanthate	350	41	40	19
<i>sec</i> -Butyl vinyl ether	450	47	37	16
<i>sec</i> -Butyl acetamide	550	46	34	20
<i>sec</i> -Butyl amine oxide ^b	150	67	21	12
<i>t</i> -Amyl acetate ^a	400	76		24
<i>t</i> -Amyl xanthate ^b	135	53		47
<i>t</i> -Amyl vinyl ether	450	66		34
2-Octyl acetate	490	46	36	18
2-Octyl xanthate ^b	165	34	48	18

^a Averages of 2 to 4 runs; in no case did an individual run vary more than 2% from the average. ^b Liquid phase.

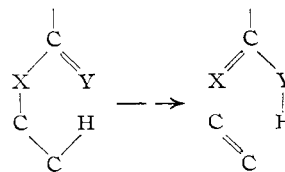
of *sec*-butyl acetate, trifluoroacetate, vinyl ether and acetamide by an internal competition method and these results are collected in Table IV. The increase in rate of only a factor of ten in changing from the acetate to the trifluoroacetate again points up the relative insensitivity of ester pyrolyses to inductive effects. The amide is much less reactive than the ester as had been noted qualitatively previously.^{6,7} Esters and vinyl ethers have approximately the same reactivity.¹¹ Consideration of these results together with the known ease of pyrolysis of xanthates strengthens the proposal

TABLE IV

RELATIVE RATES OF PYROLYSIS OF 2-BUTYL DERIVATIVES

Compound	Relative rate
Acetamide	0.04
Acetate	1
Vinyl ether	1.3
Trifluoroacetate	10

that the rate of pyrolytic elimination is roughly proportional to the change in bond energies involved in the reaction.



As a final point we investigated the product distribution in the pyrolysis of a number of 2-acetoxy-*n*-alkanes. The results of these pyrolyses are recorded in Table V. It is clear that the approximately statistical olefin distribution observed with *sec*-butyl acetate no longer obtains as the chain length increases. The amount of 1-olefin decreases to about 48 ± 2% for acetates above butyl. This decrease can be accounted for

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

(15) G. G. Smith and W. H. Wetzel, *J. Am. Chem. Soc.*, **79**, 875 (1959).

by a consideration of transition state eclipsing effects in a manner analogous to that proposed by Benkeser¹⁶ for the pyrolysis of ethylneopentylcarbinyl acetate.

In summary, this work contrasts for the first time a variety of pyrolytic *cis* eliminations in the same systems, and emphasizes again the concerted nature of these eliminations and the absence of large effects due to changes in substituents. The relative reactivity of various derivatives toward pyrolytic decomposition has been determined and shown to correlate roughly with changes in bond energies between initial and final states. This result is in agreement with a picture in which the transition state exhibits appreciable double bond character.

TABLE V

RELATIVE PERCENTAGES OF OLEFINS FORMED IN THE PYROLYSIS OF 2-*n*-ALKYL ACETATES^a

Acetate	1-Olefin, %	<i>trans</i> -2-Olefin, %	<i>cis</i> -2-Olefin, %
2-Butyl	57	28	15
2-Pentyl	51	34	15
2-Hexyl	48	37	15
2-Heptyl	49	33	18
2-Octyl	46	36	18

^a Average of 2 to 4 runs; in no case did an individual run vary more than 2% from the average.

Experimental

Esters and amides were either commercial materials or were prepared from the corresponding amine or alcohol by reaction with the appropriate acid chloride or anhydride. In all cases the physical properties checked with literature values where available. Purity was also determined by gas chromatography.

Vinyl ethers were prepared by the method of Watanabe and Conlon.¹³ A solution of mercuric acetate (3 g.), *sec*-butyl alcohol (37 g., 0.5 mole) and ethyl vinyl ether (144 g., 2 mole) was heated at reflux for 6 hours. Most of the excess vinyl ether was removed by distillation, the residue taken up in ether and washed well with water. Distillation gave *sec*-butyl vinyl ether, b.p. 81–83° (lit.¹⁷ 81–81.5°). For the pyrolysis experiments the vinyl ether was purified by preparative scale gas chromatography. *t*-Amyl vinyl ether was prepared by a similar procedure and also purified by preparative g.p.c.

Xanthates.—*sec*-Butyl xanthate was prepared by the Whitmore^{16,18} modification of the Chugaev reaction. In a liter flask was placed finely pulverized NaOH (20 g., 0.5 mole), ether (300 ml.), carbon tetrachloride (25 ml.) and *sec*-butyl alcohol (37 g., 0.5 mole). After reacting at zero degrees for 0.5 hour, CS₂ (38 g., 0.5 mole) was added with cooling over a period of 1 hour. The mixture was stirred for 3 hours, during which time a yellow precipitate formed. Methyl iodide (74 g., 0.5 mole) was added dropwise with cooling and the mixture heated at reflux for 7 hours. The

precipitated sodium iodide was removed by filtration and, after the removal of the solvent, the xanthate was collected by distillation, b.p. 57–59° (4 mm.).

t-Amyl xanthate was not stable to distillation and so it was prepared and pyrolyzed in solution. Potassium (8.5 g., 0.21 mole) was dispersed in xylene (150 ml.), and *t*-amyl alcohol (18 g., 0.26 mole) was added dropwise with vigorous stirring. The temperature was raised to 65° and the reaction was complete in 2 hours. The solution was diluted with 150 ml. of butyl ether and CS₂ (30.5 g.) was added dropwise. The reaction mixture was allowed to stand overnight. Then methyl iodide (57 g., 0.40 mole) was added slowly and the mixture was stirred for 6 hours. This reaction mixture was filtered and used directly in the pyrolysis reaction.

Pyrolyses.—Pyrolyses were carried out by dropping the liquids at a rate of 1–2 ml./min. into a vertically mounted, externally heated glass column packed with Pyrex helices.³ Dry purified nitrogen was passed slowly through the column and the products were collected in Dry Ice and liquid nitrogen traps. The yields were determined both titrimetrically where possible, and gravimetrically by weighing the amount of olefins produced. The two results agreed closely. When the olefinic products were butenes or pentenes, they were distilled under reduced pressure into a vacuum line and collected in gas sampling tubes. When the olefins were higher boiling, the products were taken up in ether, the acetic acid was removed by washing with bicarbonate solution and the solution was dried over sodium sulfate. *t*-Amyl xanthate and 2-octyl xanthate were pyrolyzed in the liquid phase by heating their xylene or toluene solutions and collecting the olefins produced.

Analysis of Olefins.—Olefinic products were analyzed by gas phase chromatography using a Perkin-Elmer Vapor Fractometer model 154C. A 5-meter column of dibutylformamide on Celite was used for the butenes and pentenes. For higher boiling olefins a 2-meter silver nitrate in diethylene glycol on Celite or a dimethyl sulfolane on Celite column was used.

Relative Thermal Conductivities.—As a test of the assumption that the isomeric olefins should have equal thermal conductivity, an authentic sample of *trans*-2-octene was obtained by preparative g.p.c. and mixed in known proportion with an authentic sample of 1-octene from the pyrolysis of *n*-octyl acetate. The ratio of olefins as calculated from g.p.c. analysis agreed within experimental error with the known ratio.

Relative Rates of Pyrolysis.—Relative rates of pyrolysis of *sec*-butyl trifluoroacetate *vs.* *t*-butyl acetate, *sec*-butylacetamide *vs.* *n*-butyl acetate and *sec*-butyl vinyl ether *vs.* *sec*-butyl acetate were determined by an internal competition method. As a typical example, a 3:1 molar mixture of *sec*-butyl trifluoroacetate and *t*-butyl acetate was pyrolyzed and its percentage conversion determined both by weighing the butenes and by titrating the acetic acid produced. These two results checked. The olefins produced were analyzed by gas phase chromatography and the amount of 1-butene and 2-butene *vs.* isobutene was measured. From these data, the relative rate was calculated as described by Lee.¹⁹ The relative rate of *sec*-butylacetamide *vs.* *n*-butyl acetate was determined by an analogous procedure.

For the relative rate of *sec*-butyl vinyl ether *vs.* *sec*-butyl acetate, the reactants were mixed in equimolar quantities with toluene as an internal standard, and the amount of each reactant in the mixture was measured by gas phase chromatography both before and after pyrolysis. The relative rate was then determined as above.

The relative rates of primary:secondary:tertiary acetates has been determined.^{3,8} From these data, the rates of pyrolysis of these esters relative to *sec*-butyl acetate were calculated.

(19) T. S. Lee in "Techniques in Organic Chemistry," Vol. XIII, Interscience Publishers, Inc., New York, N. Y., 1953, p. 101.

(16) R. A. Benkeser, J. J. Hazdra and M. L. Burrous, *J. Am. Chem. Soc.*, **81**, 5374 (1959).

(17) M. E. Shostakovskii, B. T. Mikhant'ev and N. N. Ovchinnikova, *Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk*, 1099 (1952); *C. A.*, **48**, 1242 (1954).

(18) F. C. Whitmore and C. T. Simpson, *J. Am. Chem. Soc.*, **55**, 3809 (1933).