PYROLYTIC CIS ELIMINATIONS[1]

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CONTENTS

I. INTRODUCTION

A number of organic molecules fragment, when heated, with the formation of an olefin. Some of these elimination reactions have been extensively investigated and a few have important synthetic utility. The recent introduction of gas-chromatographic methods of analysis has aided greatly in the elucidation of the mechanisms of the eliminations and has also allowed the accumulation of important new data on the products to be expected from these reactions. Although much is yet to be discovered about pyrolytic cis eliminations, the general mechanistic pattern of the several types can now be discerned.

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A. IMPORTANCE OF PYROLYTIC CIS ELIMINATIONS

Pyrolytic eliminations are important from both the practical and the theoretical point of view. Synthetically, the reactions are often the method of choice for the introduction of unsaturation under mild conditions and without rearrangement; in other cases the extreme simplicity of the reactions makes them attractive, problems of work-up of the reaction mixtures seldom being encountered. The products formed in pyrolytic eliminations often differ appreciably in composition from those formed in other types of eliminations, and this too is sometimes of advantage. Finally, the unique cis steric course of the reaction occasionally allows the formation of only a single product, a product which it might not be possible to form under other eliminating conditions. These, and other reasons which will become apparent, make pyrolytic cis eliminations attractive synthetic procedures.

Pyrolytic eliminations offer one of the few opportunities for the study of nonchain gas reactions and of cyclic processes. Variation of reaction rate with structure, variation of product distribution with the nature of the leaving group, the kinetic isotope effect—all these common tools of the study of organic reaction mechanisms may conveniently be applied to that of pyrolytic eliminations. As a consequence, more is known about the details of these eliminations than of any other cyclic reactions, and the conclusions reached in these studies will be of use in interpreting results obtained from analogous reactions.

B. SCOPE OF THE REVIEW

1. Nature of the groups being eliminated

Pyrolytic eliminations from four groups of compounds—esters, xanthates, amine oxides, and halides—have been extensively investigated, and this review will deal mainly with them, in the order listed. The pyrolysis of esters is discussed the most thoroughly, because the most work has been done in that system, the reaction is currently somewhat controversial, and the authors are most familiar with the field. Many topics discussed in detail with esters will be referred to more briefly with the other groups to avoid repetition. Especially will this be true with the discussions of stereochemistry, since the methods by which the various eliminations were proven to be cis are similar.

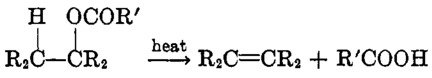
A variety of other compounds also undergo pyrolytic cis eliminations, among them vinyl ethers, amides, sulfoxides, and alcohols. Usually little is known about these reactions, or they appear to be very similar in mechanism to one of the main groups. The available data for each of these eliminations are summarized in this review, although without unwarranted discussion. Several eliminations have, at one time or another, been suggested to belong to the class of pyrolytic cis eliminations but, on further examination, have been shown to belong to some other mechanistic class. With one exception these reactions have been ignored in this review. The exception, the pyrolysis of borate esters, has been included because some of the data on which the conclusions of the authors are based have not yet been published, and the reaction is still often included among pyrolytic cis eliminations.

2. Literature coverage

The authors have tried to be selective in the literature cited in this review, limiting themselves primarily to work dealing with the mechanism and direction of pyrolytic cis eliminations. Even much recent literature is in error on the latter point; hence the authors have tried to include in the tables and text only results which they consider dependable, preferring to err on the side of omission rather than to include incorrect results. All but a few representative examples of pyrolytic eliminations in complex natural products have also been omitted, because precise quantitative work is rare in that field and it is usually hard to be sure that the reaction in question is genuinely of the desired type. An attempt has been made to give some coverage to the main types of side reactions observed in these eliminations and to point out, with appropriate examples, some of their major advantages in synthesis.

II. PYROLYSIS OF ESTERS

It has been known for over a century that an ester, when heated at 300–550°C., decomposes into an olefin and a carboxylic acid (115). The reaction may be carried out in either the liquid or the vapor phase, by simply heating the ester in a metal bath or with a free flame if its boiling point is sufficiently high, or by passing the compound through an electrically heated tube maintained at about 500°C. Where the two methods have been directly compared, the results are usually equally good, although the vapor-phase method has the advantage that the products are maintained at a high temperature for only a short period of time.



$$\overset{H}{\underset{|}{R_2C}}-\overset{OCOR'}{\underset{|}{CR_2}} \xrightarrow{\text{heat}} R_2C{=}CR_2 + R'COOH$$

The ester pyrolysis reaction is extremely simple in experimental procedure, the yields are nearly always excellent and sometimes quantitative, and the absence of solvents and other reactants makes the reaction mixtures easy to work up. When the pyrolysis of an ester is carried out in the vapor phase, the pure ester is added dropwise to the top of a vertically mounted Pyrex tube packed with glass helices or beads, and heated with a furnace for about 12 in. of its length. The diameter of the tube may vary with the size of the furnace; an internal diameter of ½ to ¾ in. is convenient. A typical apparatus for vapor-phase pyrolysis is shown in figure 1. The ester is added to the top of the column through the dropping funnel, and the products are swept from the reaction chamber by a slow stream of nitrogen and collected in a cold trap. For general preparative purposes a pyrolysis temperature of 500–525°C. is most convenient, since the conversion of secondary and tertiary esters to olefins is reasonably complete at these temperatures. Primary esters will require recycling, but this is usually preferable to the use of higher temperatures, which often lead to charring, to rearrangement of the products, or to secondary reactions. The per cent conversion in the reaction may readily be determined by titration with base of an aliquot of the product mixture, and the olefinic products may be removed by distillation or other standard methods.

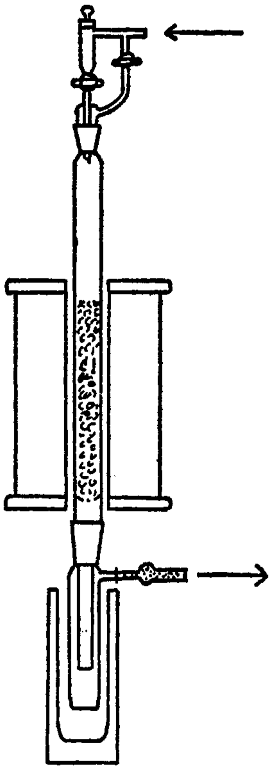
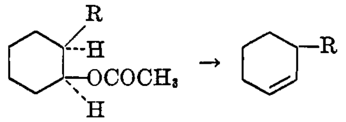
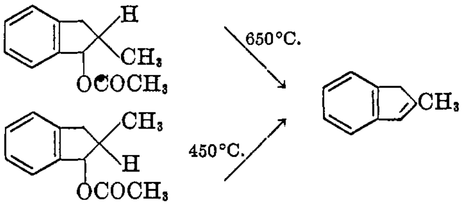


FIG. 1. A typical apparatus for vapor-phase pyrolysis.

A. STEREOCHEMISTRY OF THE REACTION

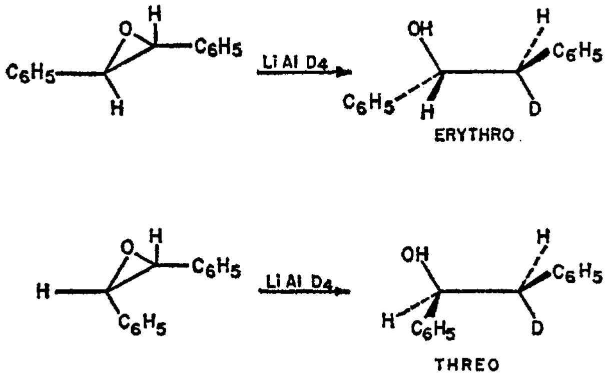
The cis character of the elimination reaction occurring in the pyrolysis of esters has been demonstrated by a number of experiments. In the simplest of these it has been shown that eliminations do not take place in the absence of a cis β-hydrogen atom, or at least are so much slower as to imply the operation of another mechanism. Thus *cis*-2-methylcyclohexyl acetate gives mainly 3-methylcyclohexene (6, 28), *cis*-2-phenylcyclohexyl acetate mainly 3-phenylcyclohexene (2), and *cis*-3-carbomethoxycyclohexyl acetate exclusively 3-carbomethoxycyclohexene (10) on pyrolysis, although in each case the trans isomer leads to mixtures of the two possible olefins. Alexander and Mudrak (3, 4) prepared the cis and trans isomers of 2-methyl-1-indanyl acetate and 2-methyl-1-tetralyl acetate and studied their ease of pyrolysis. In each case the isomer that could give olefin by a cis elimination of acetoxy and hydrogen (the trans isomer) decomposed at a much lower temperature than the isomer that could not. For example, *trans*-2-methyl-1-indanyl acetate was completely converted to olefin at 450°C., while the cis isomer required 650°C. for the same quantitative conversion.



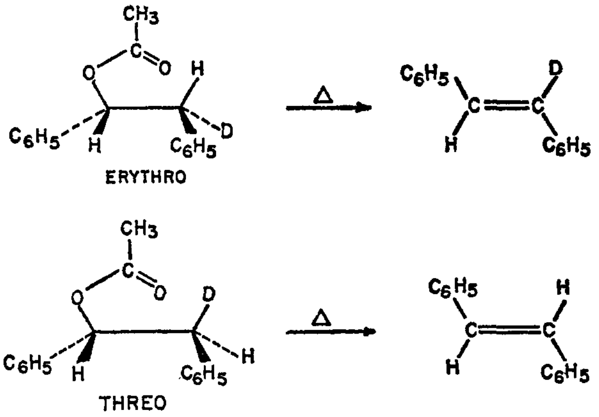


Many excellent examples of the cis nature of the ester pyrolysis reaction may be found among the steroids and other natural products. Barton (33) has summarized much of the literature in the field, and Barton and Rosenfelder (41) provided an excellent example when they found that cholestan-4(β)-yl benzoate gives exclusively 3-cholestene on pyrolysis, while its epimer gives a mixture of the 3- and 4-olefins.

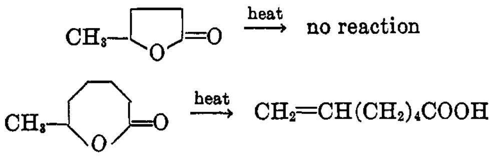
The most elegant demonstration of the cis nature of the ester pyrolysis has been provided by Curtin and Kellom (91). They prepared *threo*- and *erythro*-2-deutero-1,2-diphenylethanol by reduction by means of lithium aluminum deuteride of *cis*- and *trans*-stilbene oxide, respectively. The acetates of both of these alcohols gave *trans*-stilbene on pyrolysis, the stilbene



from the *erythro* compound retaining nearly all of its deuterium and that from the *threo* isomer having lost most of its deuterium. These results are consistent only with a mechanism for the elimination in which a cis hydrogen atom and acetoxy group are lost.

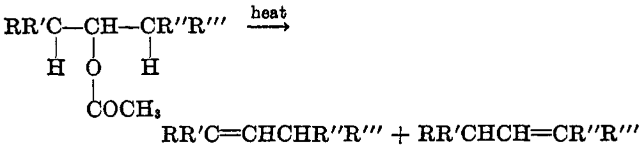


Further information about the stereochemical requirements of the ester pyrolysis is obtained from the results of Bailey and Bird (11), who observed that five- and six-membered lactones are stable to pyrolysis at 520°C., but that a seven-membered lactone and lactones containing larger rings are smoothly converted to olefins under the same conditions. Apparently only in the larger rings is there enough flexibility to allow cis attack of the carbonyl group on the adjacent hydrogen.



B. DIRECTION OF ELIMINATION

Acetates of primary alcohols must obviously decompose with the formation of a single olefin. When the acetoxy group is flanked by two or more carbon atoms bearing cis hydrogen atoms, elimination may take place in more than one direction. In order for the ester pyrolysis reaction to be generally useful, in a synthetic sense, it should be possible to predict what effect substituent groups will have on the direction of



$$\underset{\mathrm{H}}{\mathrm{RR'C}}-\underset{\underset{\mathrm{COCH_3}}{|}}{\underset{\mathrm{O}}{\mathrm{CH}}}-\underset{\mathrm{H}}{\mathrm{CR''R'''}} \xrightarrow{\text{heat}} \mathrm{RR'C{=}CHCHR''R''' + RR'CHCH{=}CR''R'''}$$

elimination. For some time it was thought that only a single product was formed in the pyrolysis of aliphatic acetates, primary olefins being formed wherever possible (23, 24, 27) (Hofmann elimination (119)). Thus 3-methyl-1-butene was reported to be the exclusive product from the pyrolysis of 3-methyl-2-butyl acetate (R, R′ = H; R″, R‴ = CH_3), and methylenecyclohexane the major or exclusive product from the pyrolysis of 1-methylcyclohexyl acetate (23, 143, 167, 178). More accurate analytical methods, especially gas chromatography, have since shown that these results are in error and that mixtures of products are ordinarily formed in the pyrolysis of esters.

1. *Aliphatic esters*

Three factors seem to be of primary importance in determining the ratios of the products formed in the pyrolysis of aliphatic esters. These are (*a*) the number of available hydrogen atoms in the various directions (statistical effect), (*b*) the repulsive interactions of groups in the transition state of the elimination (steric effects), and (*c*) the relative stability of the olefinic products formed in the eliminations (thermodynamic effects). A fourth factor, the relative acidity of the hydrogen atom removed, may become important in esters with especially activated hydrogen atoms. For simple cases, small steric and thermodynamic effects often act in opposite directions and cancel each other. In those cases the product distribution closely resembles that which would be predicted if the elimination were completely random.

(a) Statistical effects

The pyrolysis of *sec*-butyl acetate affords a particularly simple example of the operation of statistical effects. For elimination toward the methyl group, a hydrogen is cis to the acetoxy group in all rotational conformations. For elimination toward the methylene group, in one conformation there is no cis hydrogen. Consequently the formation of 1-butene is favored statistically over 2-butene by a factor of 3:2, and the product distribution, calculated statistically, is 60 per cent 1-butene and 40 per cent 2-butene, in excellent agreement with the experimental values of 57 per cent and 43 per cent. Similar arguments lead to the conclusion that in the pyrolysis of *tert*-amyl acetate the formation of 2-methyl-1-butene should be favored statistically over that of 2-methyl-2-butene by a ratio of 6 (the number of primary hydrogen atoms) to 2 (the number of secondary hydrogen

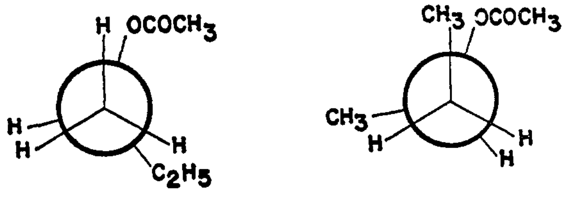


TABLE 1

Product distribution in the pyrolysis of aliphatic esters

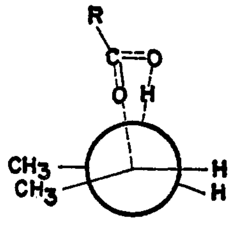
Ester	Product Distribution	References
$CH_3CH_2CH_2CH_2OCOCH_3$	$CH_3CH_2CH{=}CH_2$ (100%)	(103)
$CH_3CH_2CH(OCOCH_3)CH_3$	$CH_3CH_2CH{=}CH_2$ (57%) *cis*-$CH_3CH{=}CHCH_3$ (15%) *trans*-$CH_3CH{=}CHCH_3$ (28%)	(103, 108, 115a)
$(CH_3)_2C(OCOCH_3)CH_2CH_3$	$CH_2{=}C(CH_3)CH_2CH_3$ (76%) $(CH_3)_2C{=}CHCH_3$ (24%)	(20, 103, 148)
$CH_3CH_2CH(OCOCH_3)CH_2CH_3$	*cis*-$CH_3CH{=}CHCH_2CH_3$ (40%) *trans*-$CH_3CH{=}CHCH_2CH_3$ (60%)	(44)
$(CH_3)_2CHCH(OCOCH_3)CH_3$	$(CH_3)_2CHCH{=}CH_2$ (80%) $(CH_3)_2C{=}CHCH_3$ (20%)	(103)
$(CH_3)_2CHCH_2CH(OCOCH_3)CH_3$	$(CH_3)_2CHCH_2CH{=}CH_2$ (46%) $(CH_3)_2CHCH{=}CHCH_3$ (54%)	(103, 159)
$(CH_3)_2CHC(OCOCH_3)(CH_3)_2$	$CH_2{=}C(CH_3)CH(CH_3)_2$ (88%) $(CH_3)_2C{=}C(CH_3)_2$ (12%)	(20, 148)
$CH_3CH_2CH(OCOCH_3)CH_2CH_2CH_3$	*cis*-$CH_3CH_2CH{=}CHCH_2CH_3$ (15%) *trans*-$CH_3CH_2CH{=}CHCH_2CH_3$ (33%) *cis*-$CH_3CH{=}CHCH_2CH_2CH_3$ (17%) *trans*-$CH_3CH{=}CHCH_2CH_2CH_3$ (35%)	(44)
$(CH_3)_3CCH(OCOCH_3)CH_3$	$(CH_3)_3CCH{=}CH_2$ (100%)	(90, 188)
$C_4H_9CH_2CH(OCOCH_3)CH_3$	$C_5H_{11}CH{=}CH_2$ (54%) *cis*-$C_4H_9CH{=}CHCH_3$ (17%) *trans*-$C_4H_9CH{=}CHCH_3$ (29%)	(159)
$C_3H_7CH_2CH(OCOCH_3)CH_2CH_3$	*cis*-$C_4H_9CH{=}CHCH_3$ (35%) *trans*-$C_4H_9CH{=}CHCH_3$ (12%) $C_3H_7CH{=}CHCH_2CH_3$ (53%)	(159)
$(CH_3)_2CHCH(OCOCH_3)CH_2CH_2CH_3$	$(CH_3)_2CHCH{=}CHCH_2CH_3$ (73%) $(CH_3)_2C{=}CHCH_2CH_2CH_3$ (27%)	(103)
$(CH_3)_2CHCH_2CH(OCOCH_3)CH_2CH_3$	*cis*-$(CH_3)_2CHCH_2CH{=}CHCH_3$ (12%) *trans*-$(CH_3)_2CHCH_2CH{=}CHCH_3$ (33%) *cis*-$(CH_3)_2CHCH{=}CHCH_2CH_3$ (5%) *trans*-$(CH_3)_2CHCH{=}CHCH_2CH_3$ (50%)	(44)
$(CH_3)_3CCH_2CH(OCOCH_3)CH_2CH_3$	*cis*-$(CH_3)_3CCH{=}CHCH_2CH_3)$ (5%) *trans*-$(CH_3)_3CCH{=}CHCH_2CH_3$ (65%) *cis*-$(CH_3)_3CCH_2CH{=}CHCH_3$ (9%) *trans*-$(CH_3)_3CCH_2CH{=}CHCH_3$ (21%)	(44)

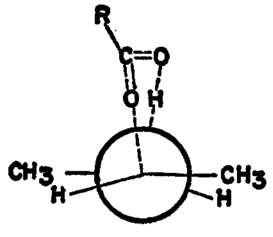
atoms). This is almost exactly the ratio found (76:24).

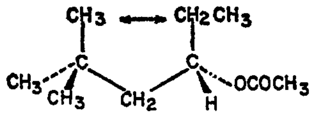
In table 1 are recorded the relative percentages of olefins formed in the pyrolysis of a number of aliphatic acetates. The product distributions have, in nearly all instances, been determined by gas chromatography and the results are felt to be trustworthy. In most cases the ratio of products formed agrees well with that expected if the elimination were random. In two cases, the pyrolysis of butyl acetate and of methyl-*tert*-butylcarbinyl acetate, only a single product would be expected. These examples are included to show the absence of rearrangement in the pyrolysis of an ester.

(b) Steric effects

Although the assumption of a completely random elimination is useful in estimating the product distribution to be expected in the case of many aliphatic esters, close examination of the data given in table 1 shows some exceptions and shows also that the agreement between calculated and actual product ratios is in part fortuitous. On statistical grounds, ethylneopentylcarbinyl acetate should form an equal mixture of the 2- and 3-olefins, and *cis*- and *trans*-2-butenes should have been formed in equal amounts from the pyrolysis of *sec*-butyl acetate. Neither of these anticipated results is actually obtained. Instead, in the cases cited, 3-olefin predominates over 2-olefin, and trans olefin over cis olefin, by a factor of about 2. These results seem most easily interpreted in terms of steric effects. Froemsdorf, Collins, Hammond, and DePuy (103) suggested that the smaller amount of *cis*-2-butene than of *trans*-2-butene formed could be due to methyl–methyl repulsion in the transition state leading to cis olefin, repulsion which is absent in the transition state leading to trans olefin. The origin of the steric effect leading to the predominance of elimination *toward* the bulky *tert*-butyl group in methylneopentylcarbinyl acetate is less obvious, but it has been pointed out (44) that a *gauche* interaction between an ethyl group and a *tert*-butyl group is relieved in the formation of a 3-olefin but not in the formation of a 2-olefin.







As a general rule, steric effects will favor the formation of primary and trans olefins and will hinder the formation of internal and cis ones. In complicated cases other, more subtle, steric effects will undoubtedly have to be taken into account.

(c) Thermodynamic effects

In general, internal olefins are more stable than their terminal isomers and, other things being equal (i.e., steric and statistical effects), the more stable isomer predominates among the pyrolytic elimination products of esters. Thus, on statistical grounds 1-butene and *trans*-2-butene should be formed from *sec*-butyl acetate in the ratio of 3:1, since eclipsing effects are absent in both cases and there are three primary hydrogen atoms whose loss would give rise to 1-butene and only a single hydrogen atom whose loss would give *trans*-2-butene. In the actual experiment the ratio formed is more nearly 2:1, the preference for the formation of more than the statistical amount of the trans isomer being ascribed to its greater thermodynamic stability. Voge and May (180) report that at equilibrium at 500°C. the butenes exist in the ratio 28 per cent 1-butene:41 per cent *trans*-2-butene:31 per cent *cis*-2-butene. Royals (159) noted that 4-methyl-2-pentene (internal olefin) predominates over 4-methyl-1-pentene (terminal olefin) in the pyrolysis of methylisobutylcarbinyl acetate, a result that may also be due to the greater stability of the 2-olefin. In no simple aliphatic system is the effect due to olefin stability very large, but it can be discerned in a number of other instances.

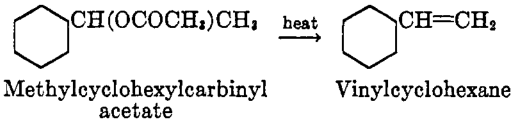
2. Alicyclic esters

In cyclic systems it becomes more difficult to treat the product distribution in terms of separate steric, statistical, and thermodynamic effects. Nevertheless, a great deal of interesting information has been deduced from such cases about the transition state for acetate pyrolysis reactions. The most instructive results are obtained in the pyrolysis of 1-methylcycloalkyl acetates (table 2), for, despite reports from four different laboratories (23, 143, 167, 178), it is now well established that 1-methylcyclohexyl acetate yields about 75 per cent 1-methylcyclohexene and only 25 per cent methylenecyclohexane. The endocyclic olefin is formed in at least this amount from the pyrolysis of 1-methylcyclopentyl and 1-methylcycloheptyl acetates. As a general rule, the formation of double bonds exocyclic to rings by the pyrolysis of esters is not favorable (46, 151, 154, 155), presumably because of their relative instability with respect to other isomers (67, 74, 179). For instance, methylcyclohexylcarbinyl acetate gives mainly a terminal olefin on pyrolysis (46).

TABLE 2

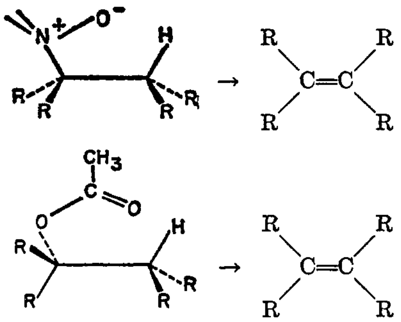
Product distribution in the pyrolysis of 1-methylcycloalkyl acetates at 450°C.

Carbon Atoms in Ring	Methylene-cycloalkane	1-Methyl-cycloalkene	References
	per cent	*per cent*	
5	15	85	(21, 100, 103)
6	25	75	(20, 43, 95, 100, 103)
7	24	76	(21, 100)



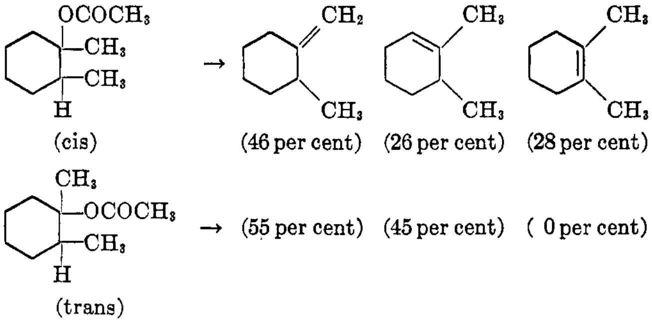
The pyrolysis of 1-methylcyclohexyl acetate deserves closer examination, since by analogy with the rigid stereochemical requirements for trans E_2 reactions it might be imagined that pyrolytic eliminations would demand a completely cis, coplanar transition state. If that were so, i.e., if the hydrogen atom and the acetoxy group had to be exactly eclipsed in the activated complex, elimination *into* the cyclohexane ring would of necessity take place through the boat conformation, for only then would perfect eclipsing be possible. On the other hand, elimination into the methyl group (to form the exocyclic olefin, methylenecyclohexane) could proceed from the lower-energy chair form. Since elimination from the boat form would require a transition state with all the steric difficulties of that system, it has been suggested (103) that a transition state is available which does not involve eclipsing, i.e., that elimination into the ring can take place directly from the chair form of the cyclohexane ring.

This explanation of the steric course of the ester pyrolysis reaction has the advantage of accounting for the remarkable difference in exo:endo product ratio between the ester and amine oxide pyrolyses in the 1-methylcyclohexyl system. In most compounds both eliminations give a very similar distribution of products, but dimethyl(1-methylcyclohexyl)amine oxide is converted to a mixture of 97 per cent methylenecyclohexane and only 3 per cent 1-methylcyclohexene. It seems probable that the extra atom in the transition state for elimination from the ester lends greater flexibility to the reaction and allows the carbonyl oxygen to reach one of the *gauche* hydrogens in the ring. In contrast, elimination from the amine oxide demands eclipsing; hence elimination into the ring, via the boat form, is unfavorable.



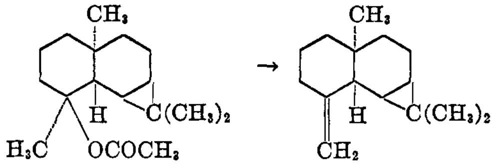
Since an axial and an equatorial acetoxy group are equidistant from a *gauche* hydrogen atom and since the same product would be formed in both eliminations, differences in the rate of pyrolysis of groups in the two positions should reflect differences in the ground-state energies of the two esters. That this is indeed the case is shown by the competitive pyrolysis of *cis*- and *trans*-4-(*tert*-butyl)cyclohexyl acetates, where the cis (axial) acetate undergoes an elimination reaction about 1.5 times more rapidly than the trans (equatorial) acetate (94).

In cyclic systems, as in acyclic ones, directive influences are rather delicately balanced and special steric situations may lead to an appreciably different product distribution. The products from the pyrolysis of *cis*- and *trans*-1,2-dimethylcyclohexyl acetates (103) are illustrative of this point, the amount of exocyclic olefin increasing in the trans compound since one mode of elimination into the ring has been removed because of an unfavorable stereochemistry (no cis hydrogen atom). The complete absence of 1,2-dimethylcyclohexene among the products of the pyrolysis of this trans compound is another example of the steric integrity of the reaction.

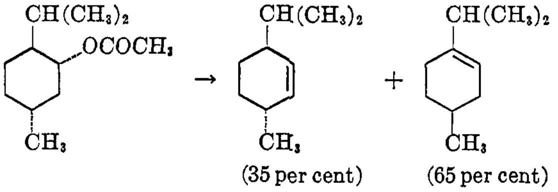


Pyrolysis of the formally similar *cis*- and *trans*-1,2-dimethylcyclopentyl acetates has also been carried out (103). In these cases the reaction is complicated somewhat by the fact that the olefins are unstable and the product ratios change with time, but it is reasonably certain that the amount of exocyclic olefin formed is small in both isomers.

In several complex systems, exocyclic isomers have been reported as the major or exclusive products of acetate pyrolyses, although in no case has the complete absence of the endo isomer been established. As a typical example, the liquid-phase pyrolysis of maali acetate (69) forms γ-maaliene, and comparable examples have been reported by Brenner and Schinz (65, 66), Ohloff and Schade (147), and others. It is not known whether conformational factors play an important part in determining exo–endo ratios.



Relatively little information is available about the direction of elimination within rings. In the cases that have been studied no dramatic effects have been observed, the more highly substituted olefin usually predominating by a small amount. Cholesteryl acetate is pyrolyzed to yield equal amounts of the Δ^2- and Δ^3-olefins (144) and methyl 3-acetoxycyclohexane carboxylate forms a mixture containing 58 per cent of the 2-olefin and 42 per cent of the 3-olefin (10). Significantly, no conjugated olefin, whose formation would have involved double-bond migration, was found among the products in the latter case. The products from the pyrolysis of a number of menthyl esters have also been accurately determined, since a ready analytical method based on the easy racemization of 3-menthene is available. The more highly substituted olefin predominates by nearly 2:1 in all these pyrolyses.



In larger ring systems an additional problem arises; both cis and trans olefins may be formed. Unfortunately the instability of the olefinic products to the reaction conditions precludes an accurate determination of the initial cis:trans ratio, but for nine- and ten-membered rings it appears probable that the trans olefin predominates (55, 57).

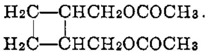
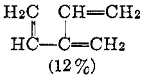
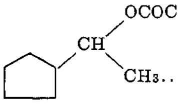
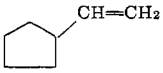
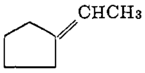
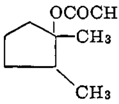
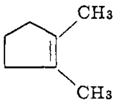
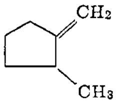
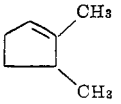
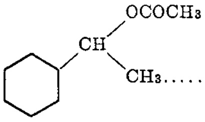
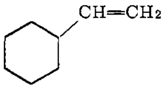
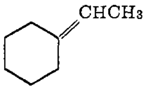
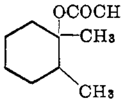
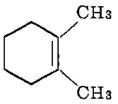
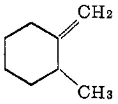
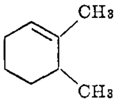
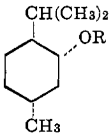
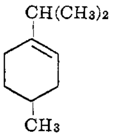
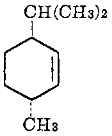
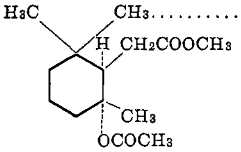
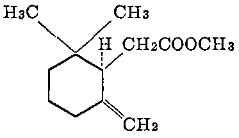
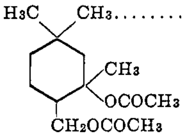
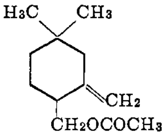
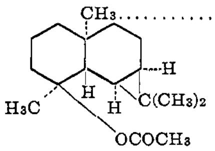
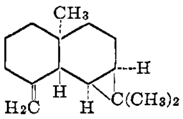
In table 3 are collected the results of the pyrolysis of a number of cyclic esters.

3. Functionally substituted esters

Functional groups exert a definite but modest effect on the direction of elimination in ester pyrolyses. The largest effect seems to be that which is observed in compounds in which the β-hydrogen atom is activated by an adjacent carbonyl group. This effect has been elegantly demonstrated by Bailey and Baylouny (10),

TABLE 3

Product distribution in the pyrolysis of alicyclic esters

Ester	Products and Yields Isolated			References
	 (12%)			(13, 58)
	 (87%)	 (13%)		(46)
				(103)
cis	(40–50%)*	(20–30%)*	(25–30%)*	
trans	(5–10%)*	(1–4%)*	(85–95%)*	
	 (90%)	 (10%)		(46)
				(103)
cis	(28%)	(46%)	(26%)	
trans	(0%)	(55%)	(45%)	
$(CH_2)_8$ $CHOCOCH_3$	$CH_2{=}CH(CH_2)_5CH{=}CH_2$ (70%)* *cis*-Cyclononene (27%)* *trans*-Cyclononene (1.5%)*			(57)
				
Acetate	(65%)	(35%)		(138, 187)
Stearate	(65%)	(35%)		(187)
Benzoate	(66%)	(34%)		(37)
Carbonate	(67%)	(33%)		(161)
S-Methylthiolcarbonate	(67%)	(33%)		(161)
	 (91%)			(147)
	 (52%)			(65)
$(CH_2)_9$ $CHOCOCH_3$	*cis*-Cyclodecene (19%) *trans*-Cyclodecene (69%)			(55)
				(69)

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* The olefin products isomerize under pyrolysis conditions.

who showed that pyrolysis of the trans isomer of methyl 2-acetoxycyclohexanecarboxylate gave the conjugated isomer almost exclusively. The conjugated ester is also the major product from the pyrolysis of β-acetoxybutyric and β-acetoxy-α-methylbutyric esters (25). If the reactions are carefully carried out in the vapor phase, no rearrangement of the double bond occurs, but in the liquid phase equilibration of the α,β- and β,γ-isomers takes place (139). There are no reliable product data for other hydrogen-acidifying groups, but Maccoll (129) has shown that the introduction of a β-carbonyl group increases the *rate* of elimination by nearly 100-fold, and it is a reasonable assumption from this result that the product is mainly conjugated olefin. The ratios of conjugated to unconjugated product obtained in these cases are in excess of those to be expected solely on the basis of differences in olefin stability and must certainly reflect a genuine effect of the acidity of the hydrogen atom being eliminated.

The influence of other functional groups has been mainly attributed to their effect on the stability of the resultant olefin, although this point cannot be considered completely settled. DePuy and Leary (96) pyrolyzed 2-acetoxy-3-(*p*-methoxyphenyl)-1-phenylpropane and showed that the olefin conjugated with the *p*-methoxyphenyl ring predominated. This olefin

$$p\text{-}CH_3OC_6H_4CH_2CH(OCOCH_3)CH_2C_6H_5 \rightarrow p\text{-}CH_3OC_6H_4CH{=}CHCH_2C_6H_5 + p\text{-}CH_3OC_6H_4CH_2CH{=}CHC_6H_5$$

(75 per cent) (25 per cent)

also predominates if the olefins are equilibrated (with base at 80°C. (120)) but is not the one to be expected if the relative acidity of hydrogen plays the dominant role. Bailey and King (25) noted that the pyrolysis of 1-phenyl-2-acetoxypropane gave a 75 per cent yield of β-methylstyrene, and that 1,1-diphenyl-2-acetoxypropane gave exclusively 1,1-diphenylpropene. Other examples of the preferential formation of substituted styrenes by the pyrolysis of esters have been reported by Overberger, Pearce, and Tanner (152) and by Alexander and Mudrak (2). It seems clear that conjugation with the developing double bond can play a role in the reaction.

In other cases in which the effect of a substituent has been assessed, DePuy, King, and Froemsdorf (95) determined the product ratios in the pyrolysis of 1-methoxy-2-acetoxypropane and showed that the amount of internal olefin increased slightly over that found for the analogous *sec*-butyl acetate.

$$CH_3OCH_2CH(OCOCH_3)CH_3 \rightarrow cis\text{-}CH_3OCH{=}CHCH_3 + trans\text{-}CH_3OCH{=}CHCH_3 + CH_3OCH_2CH{=}CH_2$$

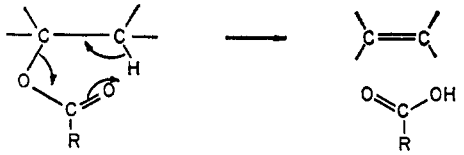
(23 per cent) (30 per cent) (47 per cent)

Burchfield (70) reported that allyl acetate is formed in 75 per cent yield from the pyrolysis of the diacetate of propane-1,2-diol.

In table 4 are summarized the reported results of the pyrolysis of functionally substituted esters.

C. MECHANISM OF THE ELIMINATION

On the basis of the stereochemistry of the reaction, Hurd (118) first suggested a cyclic, concerted (i.e., single transition state) mechanism for the pyrolysis of esters, and this now seems generally accepted as the main path for the decomposition. For primary esters and esters with no β-hydrogen atoms a radical chain decomposition has also been detected (47), and radical decompositions may be intruding, undetected, in other ester pyrolyses. The cyclic mechanism accounts well for the cis character of the reaction,



for the fact that the reaction is unimolecular, and for its negative entropy of activation. The recognition of the elimination as cyclic still leaves many questions about the transition state unanswered, and a reasonable amount of data are on hand concerning the details of the process. The data may conveniently be divided into those bearing on the breaking of the carbon–oxygen bond and those bearing on the breaking of the carbon–hydrogen bond.

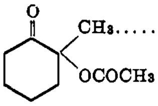
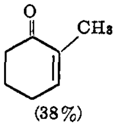
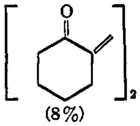
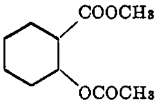
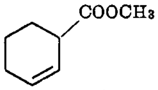
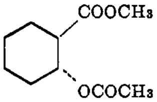
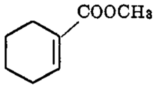
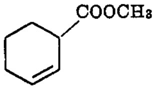
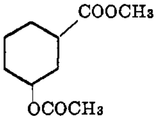
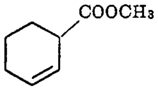
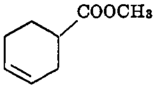
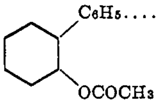
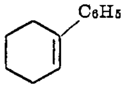
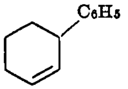
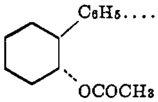
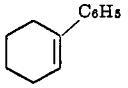
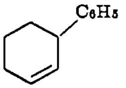
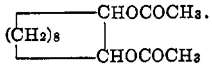
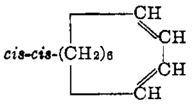
1. *Breaking of the carbon–oxygen bond*

The effect of substitution on rate can often be used to indicate the degree and type of bond breaking involved in a reaction. Ester pyrolysis reactions have been studied kinetically by several groups of workers, and the available rate data for the unimolecular, nonchain decomposition of a number of esters are collected in table 5. The relative rates of pyrolysis at 450°C. have also been computed and are recorded with the rate for ethyl acetate taken as unity. The order of reactivity, tertiary > secondary > primary, is that which would be anticipated for a reaction involving a carbonium-ion intermediate, but the actual rate differences are far too small for there to be much carbonium-ion character in the pyrolysis. If these rates were corrected for differing numbers of available hydrogen atoms and for differences in product stability, the rate increase in the series primary, secondary, tertiary would be even more modest.

More striking confirmation of the relatively small importance of carbonium-ion stability on the rate of the ester pyrolysis reaction is found in some relative

TABLE 4

Effect of substituents on the direction of elimination in the pyrolysis of esters

Ester	Products and Yields	Reference
$CH_3CH(OCOCH_3)CH_2OCH_3$	$CH_2{=}CHCH_2OCH_3$ (47%) *cis*-$CH_3CH{=}CHOCH_3$ (23%) *trans*-$CH_3CH{=}CHOCH_3$ (30%)	(95)
$CH_3COOCH_2CH(OCOCH_3)CH_3$	$CH_2{=}CHCH_2OCOCH_3$ (75%) $CH_3CH{=}CHOCOCH_3$ (25%)	(70)
$CH_3CH(OCOCH_3)CH_2COOC_2H_5$	$CH_3CH{=}CHCOOC_2H_5$	(25)
$CH_2{=}CHCH_2CH(OCOCH_3)CH_3$	$CH_2{=}CHCH{=}CHCH_3$ (64%) $CH_2{=}CHCH_2CH{=}CH_2$ (36%)	(130)
$CH_3CH_2CH_2CH(OCOCH_3)CH_2OCOCH_3$	$CH_3CH{=}CHCH{=}CH_2$ (major) $CH_3CH_2CH_2CH{=}CHOCOCH_3$ (minor)	(162)
$CH_3CH(OCOCH_3)CH(CH_3)COOC_2H_5$	*cis*-$CH_3CH{=}C(CH_3)COOC_2H_5$ (major) *trans*-$CH_3CH{=}C(CH_3)COOC_2H_5$ (minor)	(25)
	 (38%)  (8%)	(182)
	 (100%)	(10)
	 (97%)  (3%)	(10)
	 (58%)  (42%)	(10)
	 (7%)  (93%)	(2)
	 (87%)  (13%)	(2)
$C_6H_5CH_2CH(OCOCH_3)CH_3$	$C_6H_5CH{=}CHCH_3$ (75%) $C_6H_5CH_2CH{=}CH_2$ (25%)	(25)
$C_6H_5CH(CH_3)CH(OCOCH_3)CH_3$	$C_6H_5C(CH_3){=}CHCH_3$ (38%) $C_6H_5CH(CH_3)CH{=}CH_2$ (31%)	(152)
		(54)
$(C_6H_5)_2CHCH(OCOCH_3)CH_3$	$(C_6H_5)_2C{=}CHCH_3$ (98%)	(25)
p-$CH_3OC_6H_4CH_2CH(OCOCH_3)CH_2C_6H_5$	*p*-$CH_3OC_6H_4CH{=}CHCH_2C_6H_5$ (73%) *p*-$CH_3OC_6H_4CH_2CH{=}CHC_6H_5$ (27%)	(96)
p-$CH_3OC_6H_4CH_2CH(OCOCH_3)CH_2C_6H_4Cl$-*p*	*p*-$CH_3OC_6H_4CH{=}CHCH_2C_6H_4Cl$-*p* (87%) *p*-$CH_3OC_6H_4CH_2CH{=}CHC_6H_4Cl$-*p* (13%)	(96)

rate studies reported by Williams, Dunham, and Laakso (191), by DePuy, King, and Froemsdorf (95), and by DePuy and Leary (96). In the first of these studies, α- and β-phenethyl acetates and ethyl α- and β-phenethyl carbonates were pyrolyzed under identical conditions and the percentage conversion to olefin was determined. For both the acetate and the carbonate the α-phenyl ester was only about seven times more reactive than the β-phenyl one, far too small a difference for carbonium-ion character to be of primary importance. In the second study a series of esters was compared against 5-nonyl acetate as an internal standard and relative rates of pyrolysis were determined. The results, shown in table 6, again suggest that relative carbonium-ion stabilities play a negligible role in determining the rate of elimination.

TABLE 5

Arrhenius parameters and relative rates of pyrolysis of esters

Compound	E_A	$10^{-12}A$	Relative Rate at 400°C. ($C_2H_5OOCCH_3$ = 1)	References
	kcal./mole	*sec.*$^{-1}$		
C_2H_5OOCH	44.1	0.21	0.76	(49)
$C_2H_5OOCCH_3$	48.0	5	1	(49, 51)
$C_2H_5OOCC_2H_5$	48.5	5.2	0.70	(51)
iso-C_3H_7OOCH	44.2	2.7	9.1	(5, 49)
iso-$C_3H_7OOCCH_3$	45.0	10	19	(49)
tert-$C_4H_9OOCCH_3$	40.5	22	1170	(160)
tert-$C_4H_9OOCC_2H_5$	39.2	6	850	(183)
Menthyl benzoate	38.1	0.1	32	(37)
Di-2-ethylhexyl sebacate	47.1	2.7	1.05	(170)
Cholesteryl acetate	44.1	5	18	(145)
Cholesteryl methyl carbonate	41.0	2.4	89	(145)

TABLE 6

Relative rates of ester pyrolysis at 400°C. (95)

Compound	Relative Rate	Compound	Relative Rate
5-Nonyl acetate	1	β-Phenethyl acetate	0.07
α-Phenethyl acetate	0.74	α-Acetoxycyclohexanone	0.06

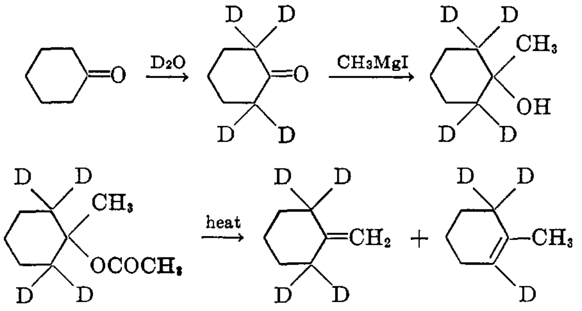
DePuy and Leary showed that a *p*-methoxybenzyl acetate was only slightly more reactive than an analogous unsubstituted benzyl acetate, even in a liquid-phase pyrolysis.

Some semiquantitative work has been done on the effect of the strength of the eliminated acid on the rate of pyrolysis. The results show that the reaction is faster for esters of stronger acids. Bailey and Hewitt (22) measured the per cent conversion to olefin under standard conditions of twelve esters of 4-methyl-2-pentanol. Seven different fatty esters had identical rates (68 per cent conversion), chloroacetate was faster (87 per cent), and aromatic esters were intermediate in rate (benzoate, 73 per cent; *p*-chlorobenzoate, 77 per cent; *p*-methoxybenzoate, 71 per cent) except for the *p*-nitrobenzoate, which was very fast (93 per cent) and led to extensive charring. The methyl carbonate was also fast, giving 92 per cent conversion. These authors showed that a plot of the per cent conversion *versus* dissociation constant of the acid approximated a straight line, although it is not clear what the significance of such a relation might be.

Smith and Wetzel (169) have also studied the effect of acid strength on the ease of pyrolysis, in their case the pyrolysis of cyclohexyl esters. Again esters of stronger acids were shown to undergo elimination reactions more easily than esters of weaker acids, and a correlation between acid strength and pyrolysis temperature was noted. Interestingly, *o*-substituted benzoates were considerably more stable than would be expected from their acidity, and a better correlation was found between the temperature of pyrolysis (actually the so-called "characteristic temperature," defined as the temperature at which a maximum is obtained from a plot of percentage yield divided by the pyrolysis temperature vs. the pyrolysis temperature (168, 169)) and the relative rates of alkaline hydrolysis of the esters, or between temperature and the position of the carbon–oxygen stretching band in the infrared spectrum. Despite the fact that an increase in acid strength leads to an increase in the rate of pyrolysis, the product distribution is very little affected. DePuy, Bishop, and Goeders (93) have studied the pyrolysis of *sec*-butyl acetate, formate, benzoate, monochloroacetate, dichloroacetate, and trifluoroacetate. The latter three esters are particularly easily pyrolyzed, yet the ratio of 1-butene:*trans*-2-butene:*cis*-2-butene does not change much from that found for the acetate.

2. Breaking of the carbon–hydrogen bond

Acidification of a β-hydrogen atom by the introduction of a carbonyl group adjacent to it substantially increases the rate of ester pyrolysis (*vide supra*). In unactivated cases the relative acidity of the hydrogen atom has little influence, as shown by the results for the pyrolysis of 1,3-diphenyl-2-propyl acetate (96) and of 1-methoxy-2-acetoxypropane (95). The most direct measure of the importance of the breaking of the carbon–hydrogen bond in the transition state of a reaction can be obtained by the effect on the rate of replacing hydrogen by deuterium (189). Curtin and Kellom (91) first obtained the kinetic isotope effect in acetate pyrolysis during the course of their study of the stereochemistry of the reaction, using the *threo*- and *erythro*-2-deutero-1,2-diphenylethyl acetates. Using an all-aliphatic system, DePuy, King, and Froemsdorf (95) obtained a somewhat lower value. The scheme used was based on an internal competition method, as outlined below.



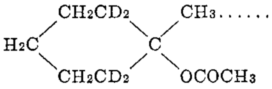
Making the reasonable assumption that the difference in rates of formation of the exocyclic olefins in the deuterated and undeuterated molecules is negligible,

k_H/k_D can be obtained directly from gas-chromatographic analysis of the reaction products.

The deuterium isotope effect has been determined in still other ways by Blades (51), who measured the absolute rates of elimination of ethyl acetate and ethyl-1,1,2,2,2-d_5 acetate, and who also pyrolyzed ethyl-1,1,2,2-d_4 acetate and determined k_H/k_D by internal competition. The first of these methods is especially important, since it is the only one that proves conclusively that the carbon–hydrogen bond is broken in the rate-determining step. It has the disadvantage that secondary deuterium isotope effects, due to rehybridization of the four unreacting deuterium atoms, would be expected to be appreciable. The isotope effects as determined by these different methods are compared in table 7. A value of about 2 at 400–500°C. seems to be most likely. Although the numbers differ somewhat in magnitude, all of them indicate a large amount of breaking of the carbon–hydrogen bond in the transition state, for the theoretical maximum value of k_H/k_D at this temperature, assuming loss of only one stretching vibration, is 2.1 (45, 189). DePuy, King, and Froemsdorf (95) suggested that the value of 1.7 obtained in the 1-methylcyclohexyl system, since it is significantly less than the maximum at the temperature studied, might fit in well with a highly concerted transition state in which the developing O—H bond compensates, in part, for the breaking of the C—H bond. In view of the disagreement as to the best value for k_H/k_D, this extension may be premature.

TABLE 7

Deuterium isotope effect in the pyrolysis of esters

Compound	Temperature	Isotope Effect k_H/k_D*	Reference
	°C.		
$C_6H_5CHDCH(OCOCH_3)C_6H_5$	400	2.8	(91)
	400 500	1.9 1.7	(95) (95)
$CD_3CD_2OCOCH_3$	500	2.1	(51)
$CHD_2CD_2OCOCH_3$	500	2.0	(51)

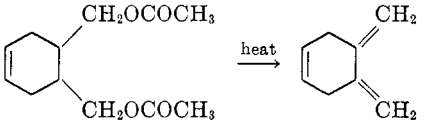
* k_H/k_D = 2.1 at 500°C. and 2.3 at 400°C. for complete loss of C—H stretching vibration (45, 189).

It has been suggested (128, 129) that the ester pyrolysis reaction owes its primary driving force to a nucleophilic attack of the carbonyl oxygen on the β-hydrogen atoms, leading to a quasi-E_2 elimination in the gas phase. If this were so, haloacetates should be less reactive than unsubstituted esters, since the carbonyl oxygen would be less basic, and vinyl ethers, in which the carbonyl group has been replaced by C=CH$_2$, should be less reactive than acetates. Both these suppositions are contrary to fact, and the experimental evidence suggests that the basicity of the attacking atom is of minor importance.

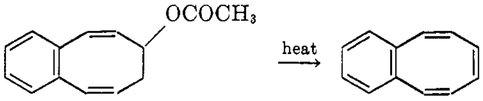
The best picture that can be drawn of the transition state for the pyrolysis of esters from the data presently at hand is that of a highly concerted elimination with only a small amount of charge separation, in which some double-bond character has developed between the carbon atoms. The transition state will make moderate use of opportunities for electron delocalization by resonance or induction, but such delocalization is not necessary for the reaction to proceed readily and results in only a modest increase in rate. These characteristics are in striking contrast to those for ionic liquid-phase reactions, where large effects of structure on rate are the rule.

D. UTILITY OF THE PROCESS IN SYNTHESES

In addition to its usefulness in preparing pure primary olefins (from primary acetates) or mixtures of olefins (from secondary and tertiary acetates), other, more specific uses of the pyrolysis of esters have been developed. Because the reaction does not involve either acidic or basic reagents, the method is especially good for preparing strained, highly reactive dienes and trienes (17, 18, 19, 26). An example is the preparation of 4,5-dimethylenecyclohexene (29), which may be formed without extensive rearrangement to the isomeric o-xylene. Wittig, Eggers, and Duffner (193) have used the pyrolysis of an ester for the preparation of benzocycloöctatetraene.

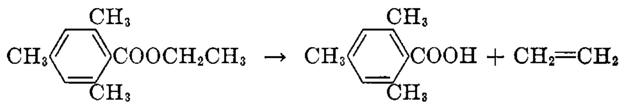


4,5-Dimethylene-cyclohexene



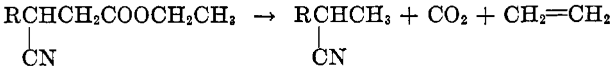
Benzocycloöcta-tetraene

Pyrolysis has many advantages over hydrolysis in the conversion of an ethyl ester to the corresponding acid, particularly if the acid is water soluble or sterically hindered. For instance, ethyl 1,3,5-trimethylbenzoate is smoothly converted (91 per cent



Ethyl 1,3,5-trimethylbenzoate

yield) to the hindered acid on pyrolysis (31), while normal hydrolysis is exceedingly difficult. A further ingenious use of the ester pyrolysis reaction is in the pyrolysis, with simultaneous decarboxylation, of β-cyano (16), β-keto (15), or malonic (14) esters. Normal hydrolysis of these compounds often leads to competing reactions and the yields are usually superior by the pyrolytic method.

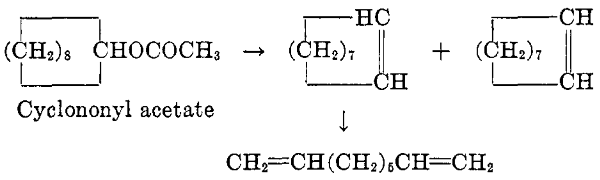


$$\underset{\displaystyle CN}{RCHCH_2COOCH_2CH_3} \rightarrow \underset{\displaystyle CN}{RCHCH_3} + CO_2 + CH_2{=}CH_2$$

In addition, the pyrolytic method is more convenient and can readily be applied to large amounts of material.

E. SIDE REACTIONS

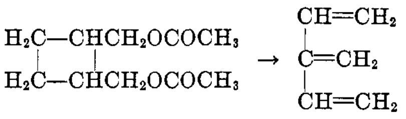
Although a number of sensitive olefins have been prepared by the pyrolysis of esters and rearrangements characteristic of acidic dehydrations are usually not found, side reactions are not completely absent in these eliminations. The most common complication is that the olefinic product formed is not stable at the high temperatures required for the reaction. Many examples of this have been reported. Blomquist and Taussig (57) studied the pyrolysis of cyclononyl acetate and found that at 500°C. a 78 per cent yield of olefin was obtained, but only 30 per cent of this product was the expected mixture of the *cis*- and *trans*-cyclononenes, the remainder being 1,8-nonadiene, formed under the conditions of the reaction by the rearrangement of *trans* (but not *cis*)-cyclononene. Dimethylenecyclobutane was also not obtained by the pyrolysis of an acetate, 2-vinyl-1,3-butadiene being formed instead (58).



Cyclononyl acetate

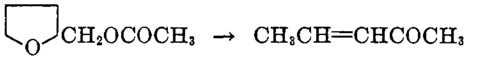
$CH_2{=}CH(CH_2)_6CH{=}CH_2$

1,8-Nonadiene



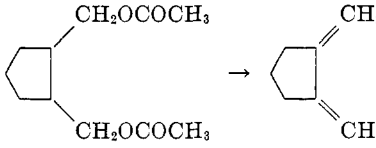
2-Vinyl-1,3-butadiene

The pyrolysis of tetrahydrofurfuryl esters has been shown to give only methyl propenyl ketone as end product (42a).



Methyl propenyl ketone

In several other cases the olefin, or more usually the diene, formed in the pyrolysis of an ester has been shown not to be as pure as the same olefin or diene formed by other eliminations. A particularly good example is the synthesis of 1,2-dimethylenecyclopentane, which has been prepared by pyrolysis of the diacetate (30, 59) and by decomposition of the quaternary base (59). The diene from the ester pyrolysis is substantially less pure than that from the base-promoted elimination. Overberger, Fischman, Roberts, Arond, and Lal (150) pyrolyzed several 2-substituted 1,4-diacetoxybutanes for the synthesis of the corresponding butadienes. When conversions were kept low to avoid formation of isomeric impurities, the reaction was an excellent one. At higher temperatures some isomerization of the double bonds took place.

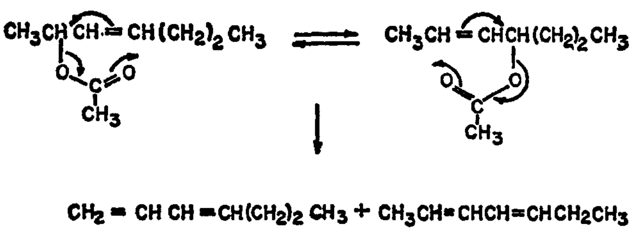


1,2-Dimethylene-cyclopentane

Occasionally the reacting ester undergoes rearrangement before the elimination, especially if it is allylic. Sometimes this rearrangement is valuable, allowing an elimination to take place where none would be anticipated. As an example, Ostromuisslenskiĭ (149) showed that crotyl acetate could be converted to butadiene on pyrolysis. More usually the rearrangement leads to mixtures of products which would not be expected. Grummitt and Splitter (107) pyrolyzed 3-acetoxy-1-cyclohexyl-1-butene and obtained an appreciable amount of diene resulting from rearrangement of the acetoxy group. Bailey and Barclay (9) studied the rearrangement and, by running the reaction at low conversion, were able to isolate ester which had undergone rearrangement but not elimination. Marvel and Brace (135) also isolated rearranged ester from an attempted elimination. Recently Greenwood (105) has provided an elegant example. He showed that 2-acetoxy-3-heptene and 4-acetoxy-2-heptene gave the same mixture of 1,3-heptadiene and 2,4-heptadiene on vapor-phase pyrolysis, indicating

$$CH_3CH{=}CHCH_2OCOCH_3 \rightarrow CH_2{=}CHCH{=}CH_2$$

Crotyl acetate 1,3-Butadiene



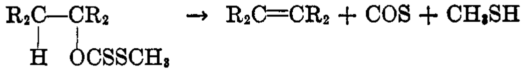
1,3-Heptadiene 2,4-Heptadiene

that equilibration of the acetates is faster than elimination. The mechanism of rearrangement is probably similar to that of elimination.

It is also clear from reports in the literature that there are conditions, as yet undefined, which promote side reactions or elimination by other mechanisms. Thus Eglinton and Rodger (100) obtained 6.5 per cent of 1-methylcyclohexene from the pyrolysis of cyclohexylcarbinyl acetate at 450°C., while Froemsdorf, Collins, Hammond, and DePuy (103) obtained only methylenecyclohexane at 530°C., and Haag and Pines (108) noted a large variation in the product ratios with per cent conversion for the pyrolysis of *sec*-butyl acetate when the pyrolysis was carried out without carrier gas, although there seems to have been no temperature effect when nitrogen was used to sweep the products through the tube. Bailey and Hale (20) have also reported a large temperature effect on the direction of elimination in ester pyrolysis. This has been disputed by other workers (51, 103), and it has been suggested (95) that traces of residual acid in the pyrolysis column might account for the predominance of Saytzeff elimination, observed at lower temperatures.

III. PYROLYSIS OF XANTHATES

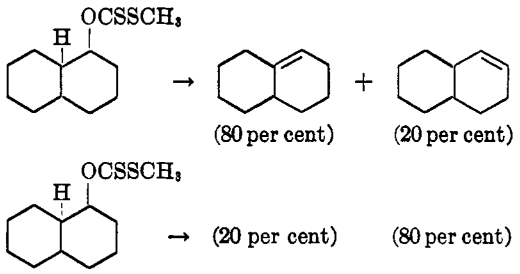
The formation of olefins by the pyrolysis of xanthates, commonly called the Chugaev reaction, has been somewhat more widely used synthetically than the pyrolysis of esters, a reaction that it closely resembles. The overall reaction involves the decomposition of a xanthate into an olefin, carbon oxysulfide, and methyl mercaptan. Like the pyrolysis of esters, the Chugaev reaction is mainly free from rearrangements and has often been applied to the formation of olefins that cannot be prepared by acid-catalyzed reactions (1, 102, 164, 181). In addition, the Chugaev reaction may be of use where the higher temperatures of ester pyrolysis cause thermal rearrangement of the products of elimination. By far the most commonly used xanthate has been the *S*-methyl derivative (R = CH_3), to which, unless otherwise specified, the term xanthate will hereafter refer.

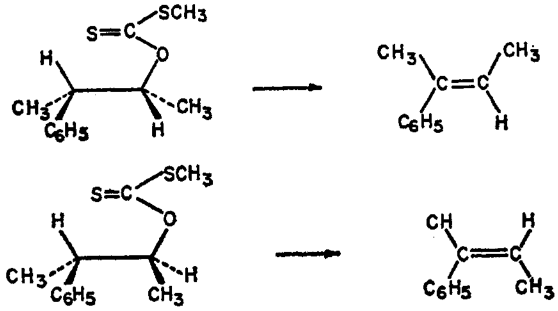


$$\underset{\displaystyle H}{R_2C}\text{—}\underset{\displaystyle OCSSCH_3}{CR_2} \rightarrow R_2C{=}CR_2 + COS + CH_3SH$$

A. STEREOCHEMISTRY OF THE REACTION

The predominant cis character of the xanthate pyrolysis was first demonstrated by Hückel, Tappe, and Legutke (117), who studied the elimination reactions of the isomeric decalyl xanthates. When a cis hydrogen atom was available, elimination took place mainly toward the ring junction, and mainly away from the ring junction when no cis hydrogen was available. These and other results from the literature were correlated and discussed by Barton (33), who showed that the stereochemistry of various natural products could be deduced from a knowledge of the stereochemistry of the Chugaev elimination. Cram (85) elegantly confirmed the stereochemistry by showing that *threo*- and *erythro*-2-butyl-3-phenyl xanthates decomposed stereospecifically, with the formation of *cis*- and *trans*-2-phenyl-2-butene, respectively.

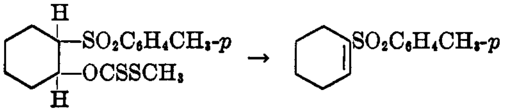




Alexander and Mudrak (2, 3, 4) studied the Chugaev reaction along with their work on the stereochemistry of ester pyrolysis, and more recently Bordwell and Landis (61) showed that *cis*-2-*tert*-butylcyclohexyl xanthate gives exclusively 3-*tert*-butylcyclohexene on pyrolysis, again indicative of a cis elimination.

The evidence quoted indicates that the predominant steric course of the Chugaev elimination is cis, but in many cases small amounts of trans elimination are also observed, indicating that the reaction is not mechanistically homogeneous. Thus up to 20 per cent trans elimination occurred in the decalols and a smaller amount of trans elimination was observed with *cis*-2-phenylcyclohexyl and 3-phenyl-2-butyl xanthates. Uncertainty about the exact purity of the starting materials and the stability of the olefins to the reaction conditions makes the amount of genuine trans elimination indeterminate.

Bordwell and Landis have recently reported that the presence of a hydrogen-acidifying group in the β-position can promote a completely trans elimination. They showed that the pyrolysis of *cis*-2-*p*-tolylsulfonylcyclohexyl *S*-methyl xanthate gives almost exclusively 1-*p*-tolylsulfonyl-1-cyclohexene by a trans elimination rather than the expected 3-isomer



1-*p*-Tolylsulfonyl-1-cyclohexene

(60). A similar result was also obtained in an acyclic system (62).

In only one case, that of *cis*-2-phenylcyclohexanol (2), have the stereospecificities of the xanthate and the acetate pyrolyses been directly compared. In that case the xanthate was reported to give 0–4 per cent, and the acetate 7 per cent, trans elimination. It is probable that more careful work could increase the specificity of both these reactions.

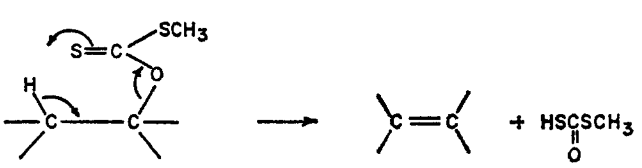
B. DIRECTION OF ELIMINATION

The direction of elimination in the Chugaev reaction has not been as extensively studied as in ester pyrolysis, but where the two reactions have been carried out in the same system the product ratios have been found to be nearly identical, despite the great differences in temperature and conditions. Literature results for the product distribution in pyrolyses of xanthates are recorded in table 8.

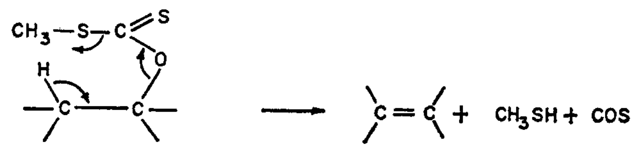
C. MECHANISM OF THE ELIMINATION

Suggestions that elimination reactions of xanthates proceed by way of prior isomerization to the isomeric dithiolcarbonates (176) have been recently disproved by the observation that these compounds are much more stable than xanthates (161), but two cyclic, concerted processes need to be considered. In the first mechanism, the analogy with the ester pyrolysis is maintained and the hydrogen is removed by the thion sulfur (C=S). This elimination step is followed by a rapid decomposition into carbon oxysulfide and methyl mercaptan.

Mechanism I:



Mechanism II:



In the second mechanism the thiol sulfur is the attacking atom, and carbon oxysulfide and methyl mercaptan are formed simultaneously with the elimination and provide an additional driving force for it. Both mechanisms have found support from various workers, but Bourns and Bader (63) have ingeniously distinguished between them by a study of kinetic isotope effects on the rates of elimination. In the study, three kinetic isotope effects were measured in the decomposition of *S*-methyl *trans*-2-methyl-1-indanyl xanthate: the S^{32}:S^{34} effect for the thiol sulfur atom, the S^{32}:S^{34} effect for the thion sulfur atom, and the C^{12}:C^{13} effect for the carbonyl carbon atom. The following predictions can be made concerning the magnitude of isotope effects to be expected for each mechanism.

I. Thiol sulfur:

Mechanism I. No, or at most a very small, isotope effect should be associated with the thiol sulfur atom, since no bond associated with this atom is broken in the rate-determining step.

Mechanism II. The bond between this sulfur atom and the carbonyl group is broken in the single-step mechanism, and this would be expected to give rise to an isotope effect ($k^{32}/k^{34} - 1$) of about 1.3 per cent.

II. Thion sulfur:

Mechanism I. The C=S bond becomes a C—S bond. Using C—S as a model for the transition state, one calculates a free-energy term of 1.0007. This will be augmented by a very small effective mass term, giving a predicted isotope effect somewhat greater than 0.7 per cent.

Mechanism II. There should be no isotope effect, since the C=S bond remains intact.

III. Carbonyl carbon:

Mechanism I. The transformation is —O—C=S to O=C—S—, and the net isotope effect should be close to zero.

Mechanism II. A single bond to this carbon is broken in the rate-determining step. This would be expected to give rise to an effect of about the same magnitude as that observed in decarbonylation reactions, i.e., 3–4 per cent.

The actual results obtained by Bourns are recorded in table 9, together with the predicted values, and it will be seen that they completely support mechanism I, a mechanism identical with that suggested for ester pyrolysis.

The direction of elimination and the mechanism of the ester and xanthate pyrolyses being so similar, the only major difference between them is the temperature required for the reaction. It is seldom possible to obtain an accurate estimate of the relative rates of elimination of a carboxylic ester and the corresponding xanthate, since the Chugaev reaction is usually carried out in the liquid phase, with consequent longer

TABLE 8

Product distribution in the pyrolysis of S-methyl xanthates

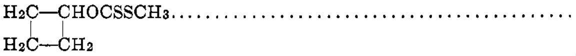
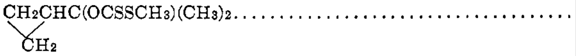
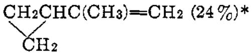
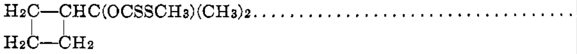
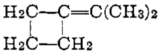
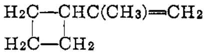
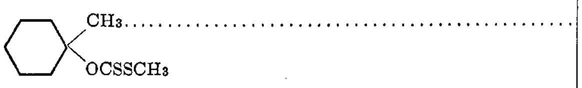
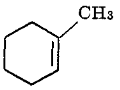
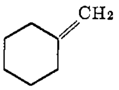
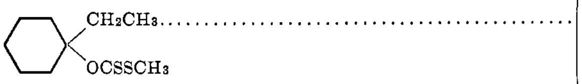
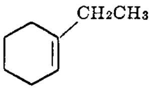
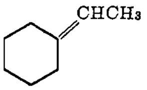
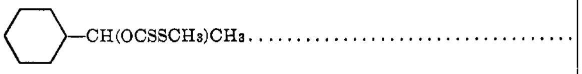
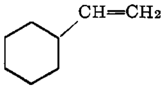
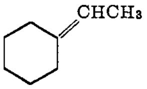
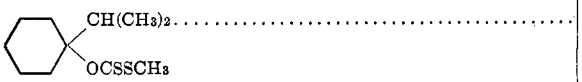
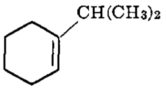
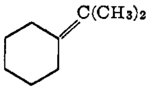
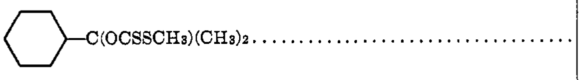
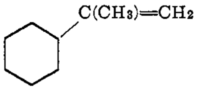
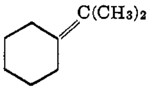
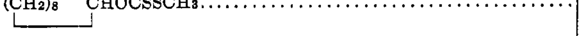
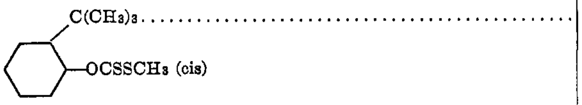
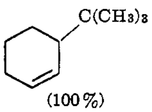
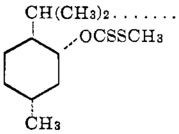
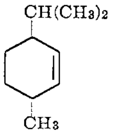
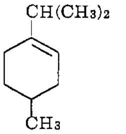
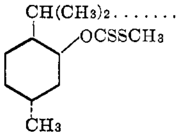
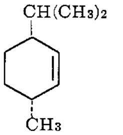
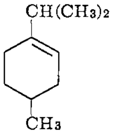
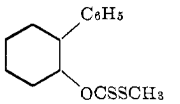
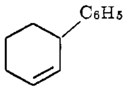
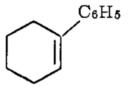
Compound	Products	References
 $H_2C—CHOCSSCH_3$ $H_2C—CH_2$	$CH_2=CHCH=CH_2$	(158)
$CH_3CH_2CH(OCSSCH_3)CH_2CH_3$	*cis*-$CH_3CH_2CH=CHCH_3$ (37%) *trans*-$CH_3CH_2CH=CHCH_3$ (63%)	(44)
$CH_3CH_2CH_2CH(OCSSCH_3)CH_2CH_3$	*cis*-$CH_3CH_2CH=CHCH_2CH_3$ (17%) *trans*-$CH_3CH_2CH=CHCH_2CH_3$ (33%) *cis*-$CH_3CH_2CH_2CH=CHCH_3$ (16%) *trans*-$CH_3CH_2CH_2CH=CHCH_3$ (34%)	(44)
$(CH_3)_3CCH(OCSSCH_3)CH_3$	$(CH_3)_3CCH=CH_2$ (100%)	(102, 164)
 $CH_2CHC(OCSSCH_3)(CH_3)_2$ CH_2	 $CH_2CHC(CH_3)=CH_2$ (24%)* CH_2	(181)
$CH_3CH(OCSSCH_3)(CH_2)_4CH_3$	$CH_2=CH(CH_2)_4CH_3$ (53%) $CH_3CH=CH(CH_2)_3CH_3$ (47%)	(186)
$(CH_3)_2CHCH_2CH(OCSSCH_3)CH_2CH_3$	*cis*-$(CH_3)_2CHCH=CHCH_2CH_3$ (6%) *trans*-$(CH_3)_2CHCH=CHCH_2CH_3$ (50%) *cis*-$(CH_3)_2CHCH_2CH=CHCH_3$ (11%) *trans*-$(CH_3)_2CHCH_2CH=CHCH_3$ (33%)	(44)
 $H_2C—CHC(OCSSCH_3)(CH_3)_2$ $H_2C—CH_2$	 $H_2C—C=C(CH_3)_2$ $H_2C—CH_2$  $H_2C—CHC(CH_3)=CH_2$ $H_2C—CH_2$	(123)
	 (79%)  (21%)	(43)
$(CH_3)_3CCH_2CH(OCSSCH_3)CH_2CH_3$	*cis*-$(CH_3)_3CCH=CHCH_2CH_3$ (2%) *trans*-$(CH_3)_3CCH=CHCH_2CH_3$ (67%) *cis*-$(CH_3)_3CCH_2CH=CHCH_3$ (6%) *trans*-$(CH_3)_3CCH_2CH=CHCH_3$ (25%)	(44)
	 (88%)  (12%)	(43)
	 (62%)  (38%)	(43)
	 (78%)  (22%)	(43)
	 (79%)  (21%)	(43)
 $(CH_2)_8\ CHOCSSCH_3$	*cis*-Cyclononene (60%) *trans*-Cyclononene (40%)	(57)
$CH_3CH(OCSSCH_3)CH(CH_3)C_6H_5$		
threo	*cis*-$CH_3CH=C(CH_3)C_6H_5$ (36%)* *trans*-$CH_3CH=C(CH_3)C_6H_5$ (11%)* $CH_2=CHCH(CH_3)C_6H_5$ (37%)*	(85)
erythro	*cis*-$CH_3CH=C(CH_3)C_6H_5$ (5%)* *trans*-$CH_3CH=C(CH_3)C_6H_5$ (49%)* $CH_2=CHCH(CH_3)C_6H_5$ (35%)*	(85)
	 (100%)	(61)

TABLE 8—*Concluded*

Compound	Products		References
	 (30%)	 (70%)	(117, 140, 161)
	 (80%)	 (20%)	(117)
$(CH_2)_9$ CHOCSSCH$_3$	*cis*-Cyclodecene (14%) *trans*-Cyclodecene (86%)		(55)
erythro-$CH_3CH_2CH(OCSSCH_3)CH(CH_3)C_6H_5$	*cis*-$CH_3CH_2CH{=}C(CH_3)C_6H_5$ (6%) *trans*-$CH_3CH_2CH{=}C(CH_3)C_6H_5$ (40%) $CH_3CH{=}CHCH(CH_3)C_6H_5$ (55%)		(85)
			
cis	(96–100%)		(2)
trans	(12%)	(88%)	
$C_6H_5CH(OCSSCH_3)CH(CH_3)C_6H_5$			
erythro	*trans*-$C_6H_5CH{=}C(CH_3)C_6H_5$ (77%)*		(88)
threo	*cis*-$C_6H_5CH{=}C(CH_3)C_6H_5$ (65%)*		
p-$CH_3C_6H_4SCH(CH_3)CH(OCSSCH_3)CH_3$			
erythro	*trans*-*p*-$CH_3C_6H_4SC(CH_3){=}CHCH_3$ (>80%)*		(62)
threo	*cis*-*p*-$CH_3C_6H_4SC(CH_3){=}CHCH_3$ (>95%)*		
p-$CH_3C_6H_4SO_2CH(CH_3)CH(OCSSCH_3)CH_3$			
erythro	*cis*-*p*-$CH_3C_6H_4SO_2C(CH_3){=}CHCH_3$ (80%) *trans*-*p*-$CH_3C_6H_4SO_2C(CH_3){=}CHCH_3$ (20%)		(62)
threo	*cis*-*p*-$CH_3C_6H_4SO_2C(CH_3){=}CHCH_3$ (95%) *trans*-*p*-$CH_3C_6H_4SO_2C(CH_3){=}CHCH_3$ (5%)		

*Yield of product isolated.

TABLE 9

Sulfur and carbon isotope effects in the pyrolysis of cyclohexyl S-methyl xanthate (63)

Isotopic Atom	Isotope Effect Predicted for		Found
	Mechanism I	Mechanism II	
	$100(k/k' - 1)$	$100(k/k' - 1)$	
Thiol S^{34}	0.0	1.3	0.21 ± 0.06
Thion S^{34}	1.0	0.0	0.86 ± 0.12
Carbonyl C^{13}	0.0	3.5	0.04 ± 0.04

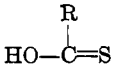
TABLE 10

Arrhenius parameters and entropies of activation of cholesteryl esters (144, 145)

Ester	E_A	$10^{-12}A$	$-\Delta S^*$
	kcal./mole	*sec.*$^{-1}$	*e.u.*
3β-Cholesteryl acetate	44.1	5.1	3.6
3β-Cholesteryl ethyl carbonate	41.0	2.4	4.3
3β-Cholesteryl *S*-methyl xanthate	32.9	2.4	4.7
3β-Cholestanyl *S*-methyl xanthate	33.8	2.0	5.0

reaction times than for the vapor-phase pyrolysis of esters. O'Connor and Nace (144, 145), however, have determined entropies and energies of activation for the pyrolytic elimination of cholesteryl esters and xanthates. The results, summarized in table 10, show that the xanthate has an activation energy 8 kcal./mole smaller than that for the carbonate. This difference in energy would correspond to a difference in rate of reaction of about 5000 at 200°C.

The much greater ease of xanthate pyrolysis as compared to the pyrolysis of esters must be due to an added driving force as a consequence of the conversion, in the transition state, of the system —O—C=S into the system O=C—S—. Summation of bond energies (153) shows that this conversion should be exothermic to the extent of nearly 20 kcal./mole, and only a part of this need be realized to account for a decrease in activation energy of 8 kcal./mole. The same argument can be put in other terms if it is recognized that the unknown acid



$$\mathrm{HO{-}}\overset{\mathrm{R}}{\mathrm{C}}\mathrm{{=}S}$$

would be very strong and that the greater ease of elimination reactions of xanthates may be thought of as a further example of the earlier generalization that esters of stronger acids are pyrolyzed more easily than those of weaker ones. This explanation accounts for the recent observations of Salomaa (161), who showed that menthyl xanthate and methyl thioncarbonate ($O—C(=S)OCH_3$) decomposed to a mixture of menthenes at the same, relatively low temperature, while the carbonate and the thiolcarbonate ($O—C(=O)$-SCH_3) were both much more stable.

Other data are available which show that, as is the case with esters, electron-withdrawing groups attached to the xanthate increase the ease of elimination. O'Connor and Nace (145) have studied the rates of decomposition of various *S*-substituted cholesteryl xanthates at 176°C. in the liquid phase. First-order rate constants for the *S*-methyl, *S*-ethyl, *S*-benzyl, *S*-diphenylmethyl, *S*-triphenylmethyl, *S*-*p*-methoxy, *S*-*p*-chloro, and *S*-*p*-nitrobenzyl derivatives were correlated with the dissociation constants of the corresponding acetic acids, giving an excellent straight line and a Hammett rho value (109, 121) for the reaction of +0.87.

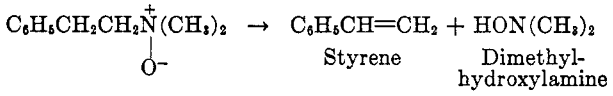
The whole problem of the ease of xanthate pyrolysis, and indeed of the mechanism of the reaction, has been somewhat confused by the recent discovery by Nace, Manly, and Fusco (140) that the so-called "stable xanthates" of McAlpine (136, 137) are in reality normal xanthates from which the last traces of peroxides have been removed. Thus menthyl xanthate, which ordinarily decomposes to a mixture of menthenes on attempted distillation, becomes distillable after washing with ferrous salt solutions and higher temperatures are required for its decomposition. Nearly identical product compositions are obtained from the pyrolysis of the "stable" and "unstable" xanthates, and the function of the peroxide is not yet clear.

D. SIDE REACTIONS

The side reactions in the Chugaev reaction are primarily those found in ester pyrolysis, but since the temperature of the reaction is much lower, changes in the products after pyrolysis are less likely. Blomquist and Taussig (57) found that whereas the pyrolysis of cyclononyl acetate gave mainly 1,8-nonadiene, the corresponding xanthate gave only *cis*- and *trans*-cyclononene at low temperatures. On the other hand, Roberts and Sauer (158) isolated only butadiene from the pyrolysis of cyclobutyl xanthate. When there is no β-hydrogen atom, other mechanisms come into play. Thus fenchyl xanthate gives cyclofenchene and rearranged α-fenchene (125, 156), and benzyl xanthate gives stilbene (126, 141).

IV. PYROLYSIS OF AMINE OXIDES

Although a few scattered references to the pyrolytic decomposition of amine oxides can be found in the early literature (98, 134, 184), the synthetic and mechanistic importance of the reaction was first recognized by Cope, Foster, and Towle (79), who showed that dimethyl(β-phenethyl)amine oxide smoothly decomposed at 85–115°C. to styrene and dimethylhydroxylamine. Since that time the reaction has found



$$\underset{\displaystyle O^-}{C_6H_5CH_2CH_2\overset{+}{N}(CH_3)_2} \rightarrow \underset{\text{Styrene}}{C_6H_5CH{=}CH_2} + \underset{\text{Dimethyl-hydroxylamine}}{HON(CH_3)_2}$$

extensive use as a means of introducing unsaturation under extremely mild conditions and is often called the Cope reaction (87).

A. STEREOCHEMISTRY OF THE REACTION

The cis steric course of the pyrolysis of amine oxides has been demonstrated by the fact that on pyrolysis neomenthyldimethylamine oxide gives only 2-menthene (73), that cycloöctyldimethylamine oxide gives only *cis*-cycloöctene (84), that *threo*-dimethyl-(3-phenyl-2-butyl)amine oxide gives mainly *cis*-2-phenyl-2-butene (and *erythro*- mainly *trans*-) (89), and that dimethyl(*cis*-2-phenylcyclohexyl)amine oxide gives 3-phenylcyclohexene (75). In all of these cases the results parallel exactly those found for the pyrolysis reactions of xanthates and acetates.

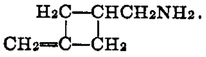
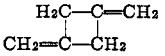
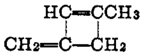
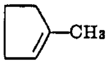
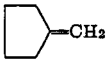
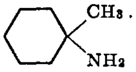
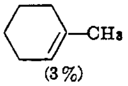
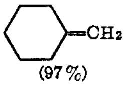
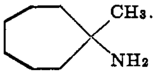
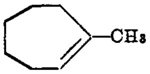
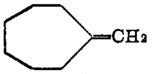
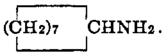
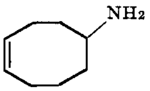
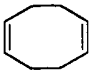
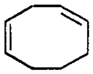
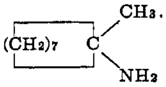
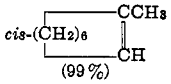
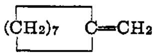
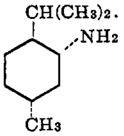
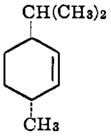
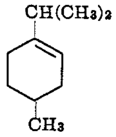
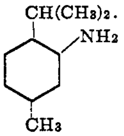
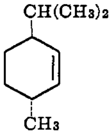
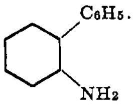
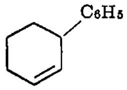
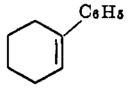
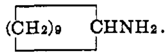
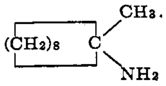
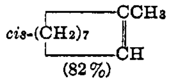
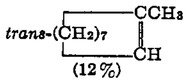
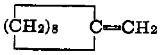
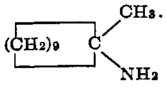
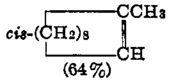
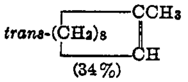
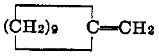
B. DIRECTION OF ELIMINATION

In the few aliphatic systems that have been studied the products from the pyrolysis of amine oxides resemble qualitatively those from the pyrolysis of esters, although amine oxides appear to be somewhat more selective. 2-Butyldimethylamine oxide, for example, gives on pyrolysis 67 per cent 1-butene, 21 per cent *trans*-2-butene, and 12 per cent *cis*-2-butene (82). The ratios for 2-butyl acetate are 57:28:15. More examples are available in cyclic systems. Of particular preparative importance is the fact that in rings of medium size the Cope elimination leads exclusively to trans olefins (83, 84). This has been suggested as a consequence of the size of the amine oxide function, which demands a quasi-equatorial conformation (87). The available data on the direction of elimination in amine oxide pyrolyses are collected in table 11.

A comparison of the products obtained in amine oxide pyrolyses with those from esters and xanthates shows many similarities and a few striking differences. The most significant difference is in the pyrolysis of dimethyl(1-methylcyclohexyl)amine oxide, which gives 97 per cent methylenecyclohexane, as compared to only 25 per cent for xanthate and ester pyrolyses in

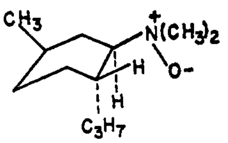
TABLE 11

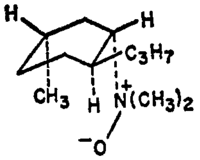
Product distribution in the pyrolysis of dimethylamine oxides

Amine	Product Distribution	References
$CH_3CH_2CH(NH_2)CH_3$	$CH_2{=}CHCH_2CH_3$ (67%) *cis*-$CH_3CH{=}CHCH_3$ (12%) *trans*-$CH_3CH{=}CHCH_3$ (21%)	(82)
$CH_3CH_2CH(NH_2)CH_2CH_3$	*cis*-$CH_3CH_2CH{=}CHCH_3$ (29%) *trans*-$CH_3CH_2CH{=}CHCH_3$ (71%)	(82)
	 (78%)  (22%)	(71, 190)
	 (97%)  (3%)	(76)
	 (3%)  (97%)	(76)
	 (85%)  (15%)	(76)
	*cis*-Cycloöctene (100%)	(84)
	 (91%)  (6%)	(80)
	*trans*-Cyclononene (100%)	(83)
	 (99%)  (1%)	(77)
$C_6H_5CH(CH_3)CH(NH_2)CH_3$		
erythro	*cis*-$C_6H_5C(CH_3){=}CHCH_3$ (4%) *trans*-$C_6H_5C(CH_3){=}CHCH_3$ (89%) $C_6H_5CH(CH_3)CH{=}CH_2$ (7%)	(89)
threo	*cis*-$C_6H_5C(CH_3){=}CHCH_3$ (94%) *trans*-$C_6H_5C(CH_3){=}CHCH_3$ (0.1%) $C_6H_5CH(CH_3)CH{=}CH_2$ (7%)	(89)
	 (65%)  (35%)	(73)
	 (100%)	(73)
	 	(75)
cis	(98%) (2%)	
trans	(15%) (85%)	
	*trans*-Cyclodecene (99%)	(83)
	 (82%)  (12%)  (6%)	(77)
	 (64%)  (34%)  (2%)	(77)

the same system. A possible interpretation of this difference, that the amine oxide (but not the ester) pyrolysis demands a cis, coplanar relationship between the hydrogen atom and the nitrogen atom, has already been discussed. This interpretation would demand that in amine oxides elimination proceeds through the boat form of the cyclohexane ring, whereas in esters eliminations can take place from the chair form. For that reason the most striking differences in product ratios in the two reactions should be found in six-membered rings. Since in five-membered rings the substituents are already approximately eclipsed, little additional activation energy is required for the formation of endo olefins. Larger rings have enough flexibility to allow eclipsing without excessive strain.

As an example of another difference between amine oxide and ester elimination which may be due to this type of interaction, eliminations in the menthyl system may be considered. Menthyldimethylamine oxide gives, on pyrolysis, 65 per cent 2-menthene and 35 per cent 3-menthene, almost exactly the reverse ratio from that found for the acetate and xanthate pyrolyses. For the latter eliminations, the larger, more flexible transition state allows elimination from the chair form, with all substituents in the equatorial position, and elimination to the more stable olefin predominates. The amine oxide reaction must take place through the boat form, and elimination toward the isopropyl group leads to unfavorable interactions between the bulky amine oxide group and the methyl group or to eclipsing between ring hydrogen atoms and the isopropyl group.





It is to be expected that the greatest differences between amine oxide pyrolyses and other eliminations will appear in systems in which eclipsing effects are the largest.

C. MECHANISM OF THE ELIMINATION

As compared to ester pyrolysis, the amine oxide elimination involves the attack on the β-hydrogen atom of a much more basic species, viz. —O⁻ instead of C═O. As a consequence, the amine oxide elimination might be expected to derive more of its driving force from the attack on hydrogen and to resemble bimolecular eliminations to a greater extent than does the pyrolysis of esters. Two lines of evidence support this view, although it should be emphasized that the similarities between amine oxide and ester pyrolyses are more striking than the differences.

By measuring the relative amounts of olefins formed in the decomposition of unsymmetrical amine oxides, Cope, LeBel, Lee, and Moore (82) were able to determine the relative rates of elimination from variously substituted amine oxides. The data are collected in table 12, together with similar values, where available, for the pyrolysis of esters. It is clear from these data that alkyl substitution on the carbon atom bearing the leaving group has far less effect on the amine oxide reaction than it does on the ester elimination, indicating that heterolytic breaking of the C—N bond in an amine oxide plays far less important a role than even the minor one that breaking of the C—O bond plays in the pyrolysis of esters. When the results are corrected for the number of β-hydrogen atoms, *tert*-butyldimethylamine oxide reacts at only slightly over twice the rate of ethyldimethylamine oxide.

TABLE 12

Relative rates of elimination of various alkyl groups as olefins in pyrolyses of amine oxides and acetates (82)

Alkyl Group	Amine Oxide at 100°C.*	Acetate at 100°C.†
Ethyl	1	1
Propyl	0.60	
Isopropyl	2.64	10^2
Butyl	0.80	
Isobutyl	0.48	
tert-Butyl	6.06	10^5
Isoamyl	0.76	
Decyl	0.88	
β-Phenethyl	70	

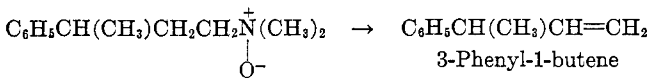
* Approximate temperature.

† Calculated from the data at higher temperatures.

Whereas substitution of the α-carbon atom has little effect on the rate of elimination, the introduction of a β-phenyl group increases the rate substantially, the relative rate, corrected for number of available hydrogen atoms, being 100 times greater for dimethyl-β-phenethylamine oxide than for ethyldimethylamine oxide. This result is in line with the greater importance of the breaking of the carbon–hydrogen bond for amine oxide pyrolyses, but it should be emphasized that in these eliminations, as in the case of esters, the dominant picture is one of a transition state with very little charge separation. How far the pyrolysis of an amine oxide is from being a true E_2 reaction can be seen in a comparison of the pyrolysis of ethylmethyl(β-phenethyl)amine oxide with that of the corresponding quaternary ammonium hydroxide. The former gives a styrene:ethylene ratio of 70; the latter a ratio of 27,000 (82).

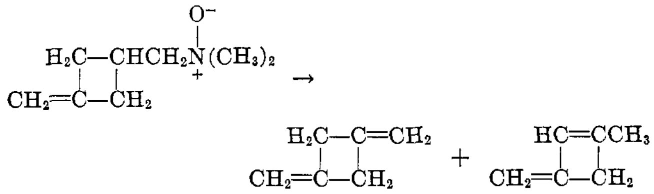
D. SIDE REACTIONS

Amine oxide pyrolyses, as compared to other elimination reactions, appear to be especially free from side reactions, and this is true for base-catalyzed rearrangements as well as those due to acid. As a particular example dimethyl(3-phenylbutyl)amine oxide gives, on pyrolysis, 3-phenyl-1-butene (86), which is completely free from its conjugated isomer, although

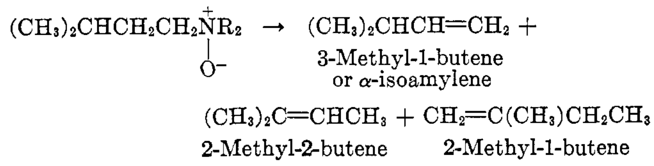


$$C_6H_5CH(CH_3)CH_2CH_2\underset{O^-}{\overset{+}{N}}(CH_3)_2 \rightarrow \underset{\text{3-Phenyl-1-butene}}{C_6H_5CH(CH_3)CH{=}CH_2}$$

the corresponding Hofmann elimination results in a considerable amount of isomeric product, and cyclobutyldimethylamine oxide gives cyclobutene rather than the butadiene obtained from other pyrolytic eliminations (158, 192). Nevertheless, side reactions do occur. In the pyrolysis of dimethyl(3-phenyl-2-butyl)amine oxide (89) and of dimethyl(*cis*-2-phenylcyclohexyl)amine oxide (75), small but detectable amounts of trans elimination took place, and in several cases involving cyclobutane rings isomerization of the double bond was observed, presumably, but not certainly, owing to migration after elimination (56, 71, 190).



A more disturbing, because less explicable, side reaction was observed by Cope, LeBel, Lee, and Moore (82), who noted that the pyrolysis of an isoamylamine oxide gave appreciable quantities of 2-methyl-2-butene and 2-methyl-1-butene in addition to the expected α-isoamylene. The olefins were shown

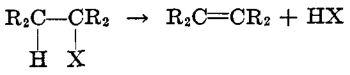


$$(CH_3)_2CHCH_2CH_2\underset{O^-}{\overset{+}{N}}R_2 \rightarrow \underset{\substack{\text{3-Methyl-1-butene}\\ \text{or }\alpha\text{-isoamylene}}}{(CH_3)_2CHCH{=}CH_2} + \underset{\text{2-Methyl-2-butene}}{(CH_3)_2C{=}CHCH_3} + \underset{\text{2-Methyl-1-butene}}{CH_2{=}C(CH_3)CH_2CH_3}$$

to be stable to the reaction conditions and the mechanism by which they are formed remains in doubt.

V. Pyrolysis of Halides

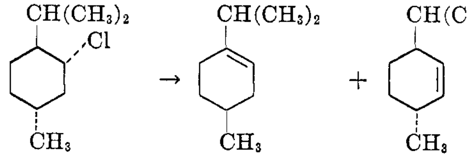
A variety of alkyl halides decompose, when heated, with the formation of olefins and hydrogen halide. When the reaction vessel is properly aged and inhibitors for the competing radical chain processes are added, a unimolecular, gas-phase elimination is observed. Although the reaction does not have the general synthetic utility of eliminations from esters and amine oxides, its kinetics have been extensively investigated and the results are pertinent to an understanding of pyrolytic cis eliminations in general.



$$\underset{H}{R_2C}{-}\underset{X}{CR_2} \rightarrow R_2C{=}CR_2 + HX$$

Although early workers had shown that alkyl halides could be decomposed to olefins (8, 142), quantitative kinetic results were generally unsatisfactory because the use of clean reaction vessels led to a predominance of heterogeneous radical reactions (127). Deposition of a layer of carbonaceous material, usually by making many runs in the same vessel, and the addition of toluene, cyclohexene, or propene as radical chain inhibitors have led in recent years to the evaluation of activation parameters for a number of pyrolytic cis eliminations from halides.

Barton, Head, and Williams (36) demonstrated the cis nature of the reaction by showing that 3-menthene was formed in 75 per cent yield by the pyrolysis of menthyl chloride.



Menthyl chloride 3-Menthene (75 per cent) (25 per cent)

In only a few other cases of unsymmetrical halides has the direction of elimination been studied: *sec*-butyl halides give 60–84 per cent of 2-butene and only 40–16 per cent of 1-butene on pyrolysis (129), and the major product from the pyrolysis of *tert*-amyl bromide is again the more highly substituted olefin, 2-methyl-2-butene (110). Apparently the Saytzeff rule is followed to a greater extent with halides than in pyrolytic eliminations involving other compounds.

The effect of alpha substitution on the rate of elimination is very much more striking for halides than it is for esters. The available Arrhenius parameters and relative rates of pyrolysis are collected in table 13. Especially significant is the rate increase in the series ethyl bromide:isopropyl bromide:*tert*-butyl bromide, which is 1:140:22,000 at 400°C. Methoxy substitution also has a dramatic effect on the rate of elimination, ethyl bromide and α-methoxyethyl bromide differing in rate by a factor of 10^6 at 400°C. (129). On the other hand, β-phenethyl chloride and bromide decompose at about the same rate as the corresponding propyl halides (129), showing that substituents that affect the breaking of carbon–hydrogen bonds do not have much effect on the rate of elimination. Consideration of the data presented has led Maccoll (129, 131) to draw an analogy between the solvolytic eliminations of halides (the E_1 reaction) and their vapor-phase pyrolysis. In this picture the rate-determining step is the heterolysis

TABLE 13

Arrhenius parameters and relative rates of pyrolysis of halides

Compound	E_A	A (× 10^{-13})	Relative Rate at 400°C.	References
	kcal./mole	*sec.*$^{-1}$		
C_2H_5Cl	59.5	16	1	(38, 129)
C_2H_5Br	53.9	2.8	12	(50, 53, 177)
iso-C_3H_7Cl	50.5	2.5	130	(34)
iso-C_3H_7Br	47.8	4.2	1660	(53, 132, 165)
C_3H_7Cl	55.0	2.8	5	(35)
C_3H_7Br	50.7	0.8	36	(53, 133)
C_4H_9Cl	57.0	10	4	(35)
C_4H_9Br	50.9	1.5	58	(133)
iso-C_4H_9Cl	56.8	11	5	(116)
iso-C_4H_9Br	50.4	1.1	63	(113)
sec-C_4H_9Cl	—	—	(500)	(129)
sec-C_4H_9Br	45.4	1.5	3600	(122, 166)
tert-C_4H_9Cl	41.4	0.25	11,800	(39)
tert-C_4H_9Br	42.2	10	260,000	(111)
tert-$C_5H_{11}Br$	40.5	4	370,000	(110)
$CH_2{=}CHCH_2CHBrCH_3$	44.7	0.9	3600	(177)
$(CH_3)_2CBrCH(CH_3)_2$	39.0	3.5	10^6	(112)
Cyclo-$C_6H_{11}Cl$	50.0	5.9	440	(173)
Cyclo-$C_6H_{11}Br$	46.1	3.2	4500	(104)
Menthyl chloride	45.0	0.4	1300	(36)
CH_3CHCl_2	49.5	0.12	13	(38)
CH_3CCl_3	54.0	10	38	(40)
$CH_3CHBrOCH_3$	33.0	0.3	10^7	(129)
$CH_3CH_2CHCl_2$	54.9	6.3	12	(34)

of the carbon–halogen bond, giving a carbonium ion–halide ion complex, followed by loss of a proton. This view has the advantage of focusing attention on the bond-breaking process showing the greatest polar character and allows the relative order of reactivity of the various halides to be understood.

Nevertheless, two lines of reasoning support the view that breaking the carbon–hydrogen bond is important in the transition state of the reaction. In the first place, the rate differences among variously substituted halides in the gas phase are, if extrapolated to room temperature, about equal in magnitude to those found for solvolytic eliminations from the same compounds. Considering that the latter eliminations are carried out in solvents of high dielectric constant and that the solvent is intimately and, with primary halides at least, specifically involved in the reaction, similar rate differences in solution and in the gas phase would indicate vast differences in the amount of heterolysis in the two reactions, so that the relative rates observed in the gas phase could arise from transition states with only very modest charge separation.

Secondly, a slow, rate-determining ionization followed by a rapid elimination demands that replacement of the β-hydrogen atoms by deuterium should have, at most, a small secondary effect on the rate of elimination. In fact, the kinetic deuterium isotope effect is as large for halides as it is for esters, k_H/k_D being 2.2 at 500°C. for ethyl bromide and 1.8 at 690°C. for ethyl chloride and ethyl bromide (50, 129). These results imply that the breaking of the carbon–hydrogen bond is nearly complete in the transition state and support the view that pyrolyses of halides and esters are mechanistically similar.

VI. Other Pyrolytic Cis Eliminations

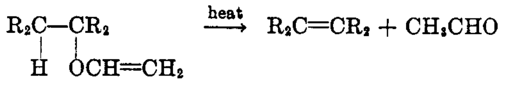
Several other types of compounds undergo concerted, cyclic, cis elimination reactions by paths which are mechanistically analogous to those suggested for esters, xanthates, amine oxides, and halides. The temperature required to bring about these reactions varies from that of boiling liquid ammonia (which hardly fits the description "pyrolytic") to temperatures higher than those required for esters. None of the methods have yet developed into widely used synthetic procedures, but some of them at least give the promise of becoming more useful in the future.

A. PYROLYSIS OF AMIDES

Olefins are formed from the pyrolysis of suitable amides, the temperature required for the pyrolysis being usually about 100°C. higher than that needed for the corresponding acetate (12, 42). The product distribution is, in the few cases studied, nearly the same as that from the acetates; *N*-(1-methylcyclohexyl)acetamide gives methylenecyclohexane and 1-methylcyclohexene in the ratio 72:28 (21, 42). Fanta has observed what are probably intramolecular pyrolyses of amides in the decomposition of the acetamides of isobutylenimine (101) and in an alicyclic analog (175).

B. PYROLYSIS OF VINYL ETHERS

Vinyl ethers decompose at about the same rate as do esters, with the formation of acetaldehyde and



$$\underset{H}{R_2C}{-}\underset{OCH=CH_2}{CR_2} \xrightarrow{\text{heat}} R_2C{=}CR_2 + CH_3CHO$$

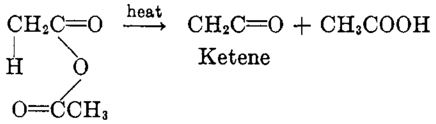
olefins. The reaction has been studied kinetically; for the decomposition of ethyl vinyl ether the energy of activation is 43.8 kcal./mole (52). Isopropyl vinyl ether has also been studied (48). The similarity in rates between esters and vinyl ethers suggests that nucleophilic attack on the hydrogen is not particularly important in determining the rate of the reaction. In two cases the product distribution has been determined (92): *sec*-butyl vinyl ether forms 47 per cent of 1-butene, 37 per cent of *trans*-2-butene, and 16 per cent of *cis*-2-butene, while *tert*-amyl vinyl ether gives a 66 per cent yield of 2-methyl-1-butene and a 34 per cent yield of 2-methyl-2-butene. Both these eliminations result in significantly more Saytzeff elimination than occurs with the corresponding acetates.

C. PYROLYSIS OF ALCOHOLS

Primary and secondary alcohols decompose mainly by radical chain processes, but for *tert*-butyl and *tert*-amyl alcohols a cyclic, unimolecular decomposition similar to that for halides has been proposed (163). Barnard (32) has recently determined that the activation energy for the process is 54.5 kcal./mole, appreciably higher than that for the corresponding halides.

D. PYROLYSIS OF ANHYDRIDES

Szwarc and Murawski (174) have shown that acetic anhydride undergoes a cyclic elimination reaction to yield ketene and acetic acid. The reaction

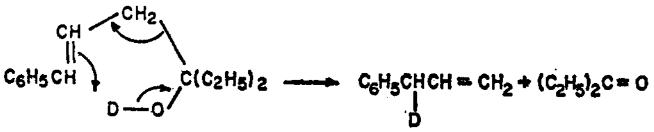


$$\underset{\mathrm{H}\quad\mathrm{O}\quad\mathrm{O{=}CCH_3}}{\mathrm{CH_2C{=}O}} \xrightarrow{\text{heat}} \underset{\text{Ketene}}{\mathrm{CH_2C{=}O}} + \mathrm{CH_3COOH}$$

($\Delta E^* = 34.5$) is 5600 times more rapid than the corresponding decomposition of ethyl acetate.

E. PYROLYSIS OF β-HYDROXYOLEFINS

Arnold and Smolinsky (7) have shown that the pyrolysis of β-hydroxyolefins is a cyclic reaction similar in mechanism to that of the pyrolysis of esters and leading to the formation of an olefin and an aldehyde. The reaction appears to be free from side reactions, since the methylenecyclohexane formed was reported to be extremely pure. When a deutero alcohol was used as starting material, deuterium was introduced into the olefinic product.



The reaction is of particular interest because it would appear to gain its primary driving force from the making of a carbon–hydrogen bond, in marked contrast to other cis eliminations.

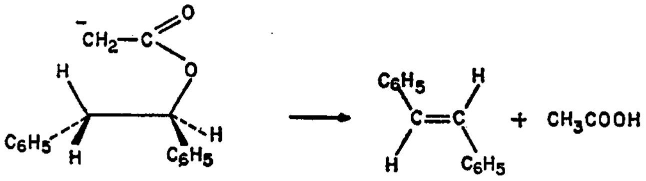
F. PYROLYSIS OF BORATE ESTERS

Brandenberg and Galat (64) first reported that alcohols could be converted to olefins by the use of boric acid or boric anhydride and showed that the borate ester was an intermediate. The analogy with ester pyrolysis was pointed out by them and by O'Connor and Nace (146). These latter authors applied the method to the dehydration of menthol, obtaining about 90 per cent of 3-menthene and 10 per cent of 2-menthene. The 3-menthene was mainly racemized, possibly after it was formed, since control experiments showed that it was not optically stable under the conditions of the reaction. Pyrolyses of borate esters have also been studied by Dev (97).

The isomer distribution reported for the dehydration of menthol is not one which is characteristic of ester pyrolyses in that system, and the fact that the 3-menthene was racemized, either during or after the elimination, shows that the reaction is proceeding under acidic conditions, so that an acid-catalyzed dehydration was considered to be a possibility. The fact that metaborate esters are linear and consequently unfavorable for a cyclic elimination also makes this pathway unattractive. Chapman and Borden (72) have recently shown that *tert*-butylmethylcarbinol gives rearranged products exclusively under the conditions of the borate pyrolysis, a result which also suggests that these are acid-catalyzed and not pyrolytic cis eliminations. Further evidence is supplied by the formation of 2,3-dihydropyran from both the pyrolysis of the borate and the vapor-phase dehydration of tetrahydrofurfuryl alcohol (42a), the latter presumably going via a carbonium-ion intermediate. Pyrolyses of esters in this system give, as end product, methyl propenyl ketone.

G. BASE-CATALYZED CIS ELIMINATION IN ACETATES

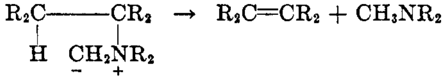
Hauser, Shivers, and Skell (114) showed that while 2-phenethyl benzoate reacted with potassium amide to form benzamide and 2-phenylethanol, the acetate under similar conditions gave styrene. Curtin and Kellom (91), using a deuterium tracer in the 1,2-diphenylethyl acetate system, showed that the reaction was cis in character and favored a cyclic mechanism.



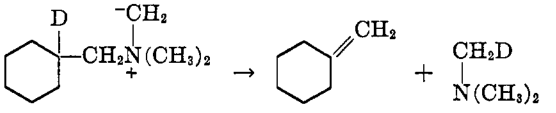
Both sets of authors pointed out, however, that this formulation may be oversimplified, since more than the single mole of potassium amide demanded by this equation seems to be required. In any event, the predominant cis nature of the reaction seems clear.

H. YLID ELIMINATIONS

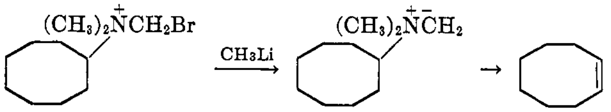
Ylids of tetrasubstituted ammonium salts may undergo a cyclic, cis elimination by a mechanism completely analogous to that by which amine oxides decompose (157, 194). Cope and LeBel (81) demonstrated that a β-deuterium atom appeared, after elimination, in the trimethylamine and that therefore the eliminating base was indeed the CH_2 group of the ylid and not phenyllithium.



$$\mathrm{R_2\underset{H}{C}\!-\!\!-\!\!\underset{\underset{-}{C}H_2\underset{+}{N}R_2}{C}R_2 \rightarrow R_2C{=}CR_2 + CH_3NR_2}$$



The ylid may be prepared by halogen–metal interchange, as was done in the preparation of cycloöctene by the reaction of dimethylbromomethylcycloöctylammonium bromide with methyllithium. The product was a mixture of 90 per cent cis and 10 per cent trans olefin. The ylid elimination has also been used

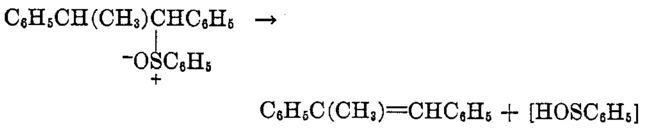


Cycloöctene

in the synthesis of bicycloöctadiene (106), and evidence has been presented that a minor part of the Hofmann elimination reaction may proceed through an ylid intermediate (185).

I. PYROLYSIS OF SULFOXIDES

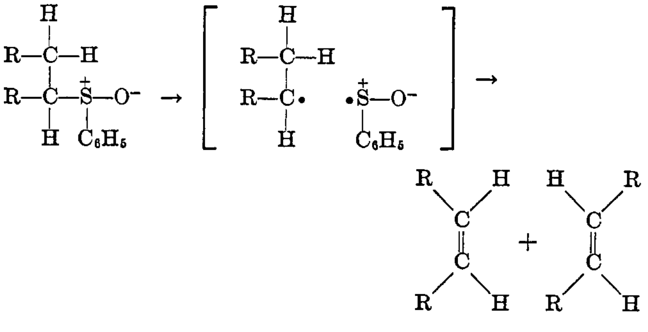
Kingsbury and Cram (124) have recently studied the first cases of eliminations from sulfoxides. They showed that the four diastereomeric 1,2-diphenyl-1-propyl phenyl sulfoxides (the sulfur atom is also asymmetric) underwent elimination at temperatures between 80° and 120°C. with the formation of mixtures of *cis-* and *trans*-1,2-diphenylpropenes.



$$C_6H_5CH(CH_3)\underset{\underset{+}{^{-}OSC_6H_5}}{CHC_6H_5} \rightarrow C_6H_5C(CH_3){=}CHC_6H_5 + [HOSC_6H_5]$$

1,2-Diphenylpropene

As with the corresponding amine oxide, the eliminations are predominantly stereospecific, the *erythro* isomers leading mainly to a trans olefin and the *threo* isomers mainly to a cis olefin. In all cases appreciable amounts of trans elimination occur simultaneously and the authors were able to show, by a careful kinetic investigation, that the trans elimination occurs by a competing, unimolecular mechanism. Since the stereospecificity and the rates of reaction are not dependent on the polarity of the solvent, ionic intermediates are considered unlikely and the most probable pathway for the trans elimination is considered to be a homolytic cleavage into radical pairs which undergo disproportionation within the solvent cage. The products from this disproportionation could be those expected from either cis or trans elimination, depending on the lifetime of the intermediate and on conformational stabilities within the cage. The extension of this explanation to trans (and even some cis) elimination in other pyrolyses is a distinct possibility.



VII. COMPARISON WITH OTHER ELIMINATIONS

Both the 2-butyl and the (−)-menthyl systems have attracted much attention in the study of eliminations, the first because of its simplicity and theoretical implications and the second because of the facile method of product analysis mentioned in an earlier section. The product distributions of various eliminations in these two systems are summarized in tables 14 and 15, showing clearly the family likeness of

TABLE 14

Product distributions for eliminations in the 2-butyl system

Substituent and Conditions	1-Butene	*cis*-2-Butene	*trans*-2-Butene	Reference
	per cent	*per cent*	*per cent*	
—OCOCH$_3$, 450°C.	57	15	28	(103)
—OCSSCH$_3$, pyrolysis	42	18	40	(92)
—(CH$_3$)$_2$N$^+$—O$^-$, pyrolysis	67	12	21	(82)
—Cl, pyrolysis	40	60*		(129)
—Br, pyrolysis	23	77*		(129)
—I, pyrolysis	16	84*		(129)
—NH$_2$, HNO$_2$	25	19	56	(171)
—Br, C$_2$H$_5$O$^-$	20	21	59	(193)
—OTs, solvolysis in CH$_3$COOH	10	43	47	(68)
Equilibrium at 25°C. (calculated)	2	23	75	(171)
Equilibrium at 450°C. (observed)	28	31	41	(180)

* The cis and trans olefins were observed "in equilibrium proportions."

TABLE 15

Product distributions for eliminations in the menthyl system

Substituent	Conditions	3-Menthene	2-Menthene	References
		per cent	*per cent*	
—OCOCH$_3$	450°C.	65	35	(138, 187)
—OCOC$_{17}$H$_{35}$	320°C.	65	35	(187)
—OCOC$_6$H$_5$	375°C.	66	34	(37)
—OCOOCH$_3$	330°C.	66	34	(161)
—OCOSCH$_3$	270°C.	67	33	(161)
—OCSOCH$_3$	170°C.	73	27	(161)
—OCSSCH$_3$	170°C.	72	28	(117, 161)
—Cl	350°C.	75	25	(36)
—Cl	Solvolysis in C$_2$H$_5$OH	70*	30*	(117)
—OTs	Solvolysis in C$_2$H$_5$OH	70*	30*	(117)
(CH$_3$)$_2$N$^+$—O$^-$	Pyrolysis	35	65	(73)
—(CH$_3$)$_3$N$^+$	Hofmann	13	87	(73)
—Cl	C$_2$H$_5$O$^-$	0	100	(117)
—OTs	C$_2$H$_5$O$^-$	0	100	(117)
Metaborate	270°C.	90*	10*	(146)

* Approximate.

pyrolytic cis eliminations and their points of difference from other common elimination reactions.

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