Studies in Decarboxylation. Part IX.[1] The Gas-phase Pyrolysis of Some Acids containing Two Double Bonds

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The gas-phase thermal behaviour of some acids containing cumulated and conjugated double bonds is examined. The 1,5-hydrogen shift typical of the decarboxylation of βγ-unsaturated acids is shown to obtain, and the variation of the associated Arrhenius parameters is discussed.

THE gas-phase decarboxylation of βγ-unsaturated acids has been shown to involve a unimolecular 1,5-hydrogen shift.[2] Alkyl substitution at the α-, β-, and γ-carbon atoms affects the rate of reaction showing that bond changes are taking place at these sites in the transition state.[3]

In Part VIII we initiated an inquiry into the structural variation which could be accommodated by this reaction, and showed that βγ-acetylenic acids decarboxylate by the same concerted mechanism in the gas phase.[1] We continue this inquiry in this paper, and detail the behaviour of three types of acid containing two double bonds. These are αβγ-allenic acids, βγδ-allenic acids, and the conjugated dienoic acids.

EXPERIMENTAL AND RESULTS

Preparation of Acids.—2,3-Butadienoic acid, prepared by the alkaline isomerisation of but-3-ynoic acid,[4] had m.p. 65—66° (lit.,[4] 65—66°). 4-Methylpenta-2,3-dienoic acid was prepared by the method of Jones *et al.*,[5] and had m.p. 87.5—89° (lit.,[5] 86—89°). Penta-3,4-dienoic acid was prepared by the literature method[6] and had b.p. 62° at 1.0 mmHg (lit.,[6] 127° at 13 mmHg). 2,2-*Dimethylpenta*-3,4-*dienoic acid* was prepared by a Reformatskii–Claisen reaction on prop-2-ynyl α-bromoisobutyrate using the route of Baldwin and Walker.[7] It had b.p. 68—70° at 0.8 mmHg (Found: C, 66.8; H, 8.0. $C_7H_{10}O_2$ requires C, 66.7; H, 7.9%).

2,2-*Dimethylhexa*-3,5-*dienoic Acid.*—Equimolar quantities of methyl α-bromoisobutyrate and freshly distilled crotonaldehyde in an equal volume of 1 : 1 dry ether–benzene were slowly added to a stirred suspension of activated zinc in the same solvent. The rate of addition was adjusted to maintain reflux and the mixture was refluxed for a further hour after the completion of addition. After cooling and decomposition with dilute hydrochloric acid, the organic layer was decanted and dried (Na_2SO_4). The crude solution was then slowly dripped onto excess of phosphorus pentaoxide and stirring was continued until the evolution of heat was complete. The liquid was decanted and worked up in the usual way to give methyl 2,2-dimethylhexa-3,5-dienoate, b.p. 124—126° at 4 mmHg, in 40% yield. The ester (7 g) was hydrolysed by reflux with a solution of NaOH (5 g) in water (25 ml), to give the acid, b.p. 150° at 5 mmHg, which polymerised after a few days standing at room temperature (Found: C, 68.5; H, 8.5. $C_8H_{12}O_2$ requires C, 68.6; H, 8.6%).

The structure of all the above acids was confirmed by i.r. and n.m.r. spectroscopy.

Stoicheiometry.—The acids were examined under three sets of conditions. In evacuated sealed tubes, at typically 15 cm pressure, the allenic acids polymerised and none was more than 35% decarboxylated. The conjugated acid gave over 90% CO_2 but the diene could not be detected. In the flow apparatus described previously,[1] the βγδ-allenic acids yielded diene and carbon dioxide quantitatively, but but-2,3-dienoic acid produced only one peak and the 4-methylpenta-2,3-dienoic acid polymerised. The conjugated acid gave 100% CO_2 and 70% diene.

TABLE 1

Pyrolysis of βγδ-allenic acids

$$H_2C{=}C{=}CHCR_2CO_2X \longrightarrow H_2C{=}CX{-}CH{=}CR_2 + CO_2$$

X	R	Temperature range (K)	$\Delta H^{\ddagger}$/ kJ mol^{-1}	$\Delta S^{\ddagger}$/ J K^{-1} mol^{-1}	10^3k/s^{-1} at 630 K *
H	H	665—715	162.3 ± 6.3	−48.1 ± 8	1.35, 1.78 †
H	CH_3	640—695	156.5 ± 6.3	−44.4 ± 8	6.49
D	H	675—725			0.64

* Characteristic temperature for these variations. † Runs in the presence of 500 mole % cyclohexene.

TABLE 2

Pyrolysis of βγ–δε-dienoic acids

$$H_2C{=}CHCH{=}CHC(CH_3)_2CO_2X \longrightarrow H_2C{=}CHCHXCH{=}C(CH_3)_2 + CO_2$$

X	Temperature range (K)	$\Delta H^{\ddagger}$/ kJ mol^{-1}	$\Delta S^{\ddagger}$/ J K^{-1} mol^{-1}	10^2k/s^{-1} at 691.5 K*	k_H/k_D at 691.5 K
H	673—723	188.7 ± 6.3	−8.36 ± 8	2.90, 2.94,† 4.90 ‡	
D	683—733			1.34	2.16

* Characteristic temperature. † Runs the in presence of 500 mol % cyclohexene as radical trap. ‡ Run in packed tube (*s* : *v* 13).

When subjected to flash vacuum pyrolysis at 600—650 K (0.01 Torr; contact time typically 1.5 s) all acids gave quantitative yields of carbon dioxide and hydrocarbons. These were identified by gas i.r., n.m.r., and mass spectroscopy and are listed below: buta-2,3-dienoic acid, propyne; 4-methylpenta-2,3-dienoic acid, 3-methylbut-1-yne; penta-3,4-dienoic acid, 1,3-butadiene; 2,2-dimethylpenta-3,4-dienoic acid, 4-methyl penta-1,3-diene; 2,2-dimethylhexa-3,5-dienoic acid, 5-methylhexa-1,4-diene.

Kinetics.—Owing to the above difficulties only the βγδ-allenic and the conjugated acids could be examined in the flow apparatus. First-order kinetics and the absence of significant radical mechanisms were shown by dilution with

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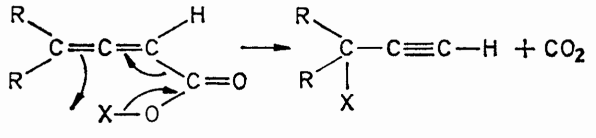
cyclohexene.[1] The activation parameters were obtained from least squares plots of log (−log a/a_0) *versus* $1/T$ after the method of Kooyman,[8] and after plotting confidence elipses of activation parameters individual rates were calculated at the temperature given by the slope of the line. The results are shown in Tables 1 and 2.

DISCUSSION

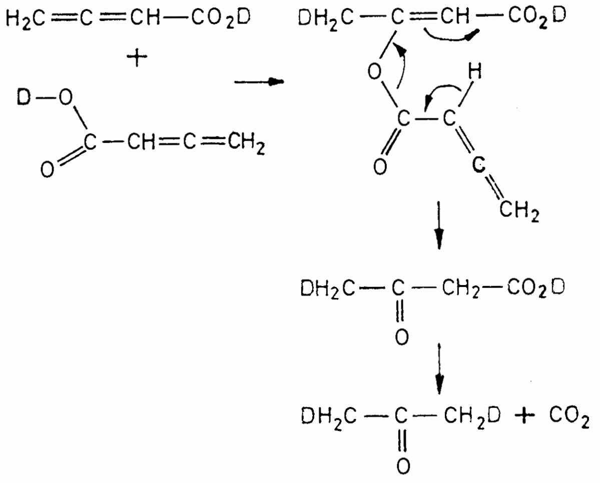
Participation of allenic bonds in electrocyclic processes has been established by several authors, most notably in the Cope [9-11] and thio-Claisen [12,13] rearrangements.

Allenic acids are a little known class of compounds. The sole report of their thermal behaviour is due to Wotiz [14] who noted that, when heated, hepta-1,2-diene-3-carboxylic acid underwent extensive polymerisation with little loss of carbon dioxide. He argued that the linear nature of the allene function precluded intramolecular attack by the carboxy-group, and resulted in intermolecular reactions. Our own results for the liquid phase are similar and we conclude that in the gas phase, polymerisation is preferred to decarboxylation. At pressures low enough to preclude intermolecular reactions and at high temperature (*i.e.* the conditions of flash vacuum pyrolysis) decarboxylation becomes the sole reaction, giving rise to quantitative yields of products. Unfortunately we were unable to examine the kinetics of the process as polymerisation persisted in our flow apparatus. However we conclude that the concerted process occurs during flash vacuum pyrolysis since a fragmentation–recombination reaction should result in some dimeric hydrocarbon and non-specific deuterium label on the acetylenes. Finally, the $C{=}C{=}C$ bending mode at 353 cm^{-1} will have a significant population of $v = 3$ with a bend of *ca.* 25° resulting in a less strained transition state (*cf.* $CH{-}C{\equiv}C$ discussed in Part VIII [1]).



R=H or CH_3 X=H or D

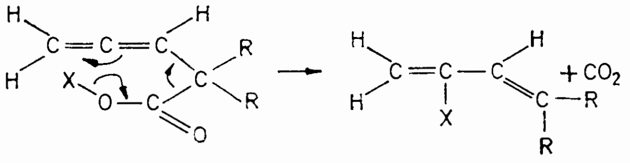
When buta-2,3-dienoic acid was heated for 2 h at 190° in a break-seal tube, and the products were transferred to a vacuum line, 35% CO_2 was found by absorption with soda asbestos, and 40% of a second product, acetone. The remnants at the bottom of the tube were sublimed to give a small amount (*ca.* 5%) of white solid, m.p. 109°, and identified by mass spectrometry as dehydracetic acid. This latter product has also been observed on heating the acid in an inert solvent [4] and parallels the reaction of its isomer, diketen. The acetone was first thought to have resulted from surface hydration of the buta-2,3-dienoic acid to acetoacetic acid. However, deuterioacetone from the pyrolysis of the allenic [^{2}H]acid when subjected to mass spectroscopy showed a symmetrical quintet based on m/e 60, indicative of the incorporation of two atoms of deuterium in each molecule of acetone. This, and the fact that the yield of no product reaches 50% suggests a bimolecular mechanism, such as dimerisation. The Scheme can account for the doubly labelled acetone.



SCHEME

Substituted acids do not appear to undergo this reaction, but differences in the behaviour of the parent acid from the rest of the series are known, *e.g.* it undergoes a Diels–Alder reaction [15] whereas 2-butylbuta-2,3-dienoic acid does not.[14]

Table 1 shows the kinetic data for the two $\beta\gamma\delta$-allenic acids studied. Activation parameters imply a concerted transition state. As with the previously studied olefinic [17] and acetylenic acids, migration of the $\beta\gamma$ π-bond occurs, in this case to give conjugated dienes as the exclusive products. The absence of radical mechanisms is indicated by the lack of effect of added cyclohexene. Runs through a packed tube (surface : volume ratio 13) in the flow apparatus were attempted. At a temperature where in the open tube 20% pyrolysis occurred, no acid was apparent through the packed tube, and the olefin peak was reduced to 5%. At 300°, when previously no carbon dioxide or diene was observed and the acid was $>97\%$ recovered, the packed tube showed no volatile



R = H or CH_3 X = H or D

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materials, but 50% of the acid was lost. Thus decarboxylation is insignificant as a heterogeneous reaction. We therefore assume that in the unpacked tube, where quantitative yields of products were obtained, the heterogeneous reaction is of little account.

Deuteriation of the parent acid gave a diene substituted on one of the two central atoms only, as expected from the concerted mechanism. A deuterium isotope effect of $k_H/k_D = 2.12$ at 630 K is evidence for the required 1,5-hydrogen shift in the transition state.

Earlier work [2] has shown that the rate of pyrolysis of βγ-unsaturated acids is altered only slightly by substitution; α-methyl groups accelerate and γ-methyl groups retard the reaction. Table 3 shows this to hold for allenic acids when the terminal methyl is exchanged for a methylene group.

TABLE 3

Rate constants (s^{-1}) and relative rates for each row ( ) and each column [ ] of pyrolysis of some unsaturated acids at 500 K

Acid	αα-Dimethyl derivative
$CH_2=CHCH_2CO_2H$ [a] $1.5_0 \times 10^{-6}$ (1.0) [7.5]	$CH_2=CHC(CH_3)_2CO_2H$ [b] $1.3_8 \times 10^{-5}$ (9.2) [10.0]
$H_2C=C=CH-CH_2-CO_2H$ [c] $3.3_5 \times 10^{-7}$ (1.0) [1.67]	$H_2C=C=CHC(CH_3)_2CO_2H$ [c] $2.1_6 \times 10^{-6}$ (6.5) [1.6]
$CH_3CH=CHCH_2CO_2H$ [d] $2.0_1 \times 10^{-7}$ (1.0) [1.0]	$CH_3CH=CHC(CH_3)_2CO_2H$ [b] $1.3_6 \times 10^{-6}$ (6.8) [1.0]
	$H_2C=CHCH=CHC(CH_3)_2CO_2H$ [c] 7.35×10^{-8} [0.054]

[a] Ref. 16. [b] Ref. 2. [c] Present work. [d] Ref. 1.

The migrating βγ-double bond is orthogonal to the γδ-double bond, and can therefore only be influenced by it inductively. The rate of pyrolysis of penta-3,4-dienoic acid is very similar to that of pent-3-enoic acid,[1] and therefore methyl and vinyl groups have the same effect on the βγ-double bond. This situation is paralleled by the similarity of rates shown by vinyl and methylcyclobutanes,[18] and by 4-bromopent-1-ene and 2-bromobutane.[19] In both cases the vinyl group is sterically precluded from mesomeric interaction with the reaction site, and can therefore interact only inductively. The similarity of rate also emphasises the rigidity of the non-planar transition state, as for this result to occur the two double bonds must remain mutually perpendicular until after the transition energy maximum or the rate should be significantly enhanced by developing conjugation.

We attempted to extend this comparison between the allenic and olefinic acids by including a β-methyl group, which strongly enhances the rate of pyrolysis of olefinic acids.[2] Ethyl 3-methylpenta-3,4-dienoate was prepared by an aliphatic Claisen rearrangement of the product of condensation of but-3-yn-1-ol and triethyl orthoacetate.[20] The ester was unstable to acid, and alkaline hydrolysis under a variety of conditions led to an inseparable mixture of the desired allenic acid with its fully conjugated isomer, 3-methylpenta-2,4-dienoic acid in a 1 : 3 ratio (n.m.r.). Pyrolysis of this mixture at 440° resulted in the decarboxylation of the allenic acid and the recovery of the conjugated isomer showing, as expected,[21] that an αβ-double bond will not participate in the decarboxylation reaction.

Table 2 shows the kinetic data for 2,2-dimethylhexa-3,5-dienoic acid. Compared with βγ-olefinic acids, this compound has an overall increase of *ca.* 30 kJ mol^{-1} in $\Delta H^{\ddagger}$ and of 30 J K^{-1} mol^{-1} for $\Delta S^{\ddagger}$, which combine to give nearly 20-fold diminution in rate (Table 3).

In the transition state for decarboxylation of the dienoic acid, the βγ-double bond is migrating, and some loss of conjugation will occur. In comparison with the olefinic acids, $\Delta H^{\ddagger}$ will be enhanced by this amount, the maximum value being 15 kJ mol^{-1}, the resonance energy of butadiene.[22] It is necessary, therefore, to postulate a second effect to account for the remainder or the whole of the difference between the two types of acid. We suggest this to be the chemical nature of 1,3-dienes where 1,2- or 1,4-addition results from terminal attack. Molecular orbital theory shows that this is due to a high electron density at the terminal atoms of the 1,3-diene system; the central atoms are correspondingly electron deficient.[22] However, the pyrolysis reaction must proceed by hydrogen transfer to one of the central carbon atoms, as shown by the specific deuterium label, and the higher value of $\Delta H^{\ddagger}$ could presumably be due to enforced reaction at the electron deficient site.

The higher entropy of activation shown by the dienoic acid may be explained in terms of developing free rotation of the δε-double bond in the transition state. This becomes an isolated vinyl group as the other double bond moves from the βγ- to the αβ-position. Benson has noted the reverse situation in comparing alkyl-substituted cyclopropanes or cyclobutanes with their vinyl substituted counterparts, where the latter compounds had lower *A* factors by a power of ten.[23] He noted that this was explicable in terms of a net loss of hindered rotation of the vinyl group amounting to *ca.* 26 J K^{-1} mol^{-1}.

[5/1754 *Received*, 12*th September*, 1975]

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