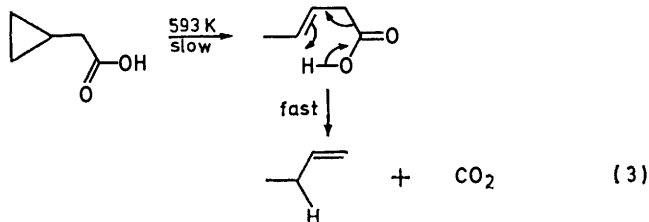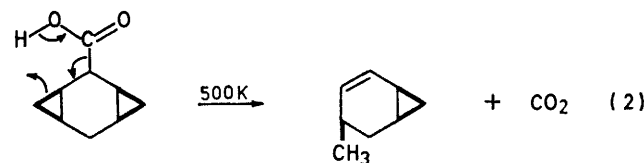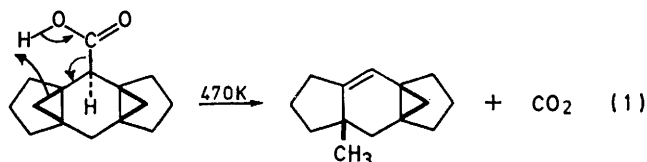# Studies in Decarboxylation. Part 12.[1] A Concerted Mechanism for the Gas-phase Pyrolysis of Cyclopropylacetic Acids

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Certain cyclopropylacetic acids are shown to decompose by a concerted mechanism, very similar to that of their βγ-unsaturated counterparts.

SOME years ago three communications concerning the thermal decomposition of cyclopropylacetic acids appeared in close order. Hanafusa et al.[2] proposed the concerted mechanism (1) for a pentacyclic acid, and

$$\text{(1)} \qquad 470\text{K} \qquad + \; CO_2$$

$$\text{(2)} \qquad 500\text{K} \qquad + \; CO_2$$

$$\text{(3)} \qquad \frac{593\,\text{K}}{\text{slow}} \qquad \xrightarrow{\text{fast}} \qquad + \; CO_2$$

Sims[3] proposed a similar mechanism (2) for a closely related tricyclic acid; neither group produced evidence in support of their mechanism nor did they consider other possible mechanisms. On the other hand, Bigley and Thurman[4] showed that cyclopropylacetic acid itself appeared to decompose via the stepwise mechanism (3) involving decarboxylation of an intermediate βγ-unsaturated acid. These authors deduced their mechanism largely by examination of the olefin from the decomposition of the carboxy-deuteriated acid. For the concerted mechanism [(1) and (2)] this should have been 4-deuteriobut-1-ene, while the stepwise mechanism was favoured by the resultant 3-deuteriobut-1-ene.

The temperature of Bigley and Thurman's experiments was close to the region for cyclopropane ring openings (650—750 K), but the other workers' temperatures fell rather short of this. This could result from ring strain facilitating the cyclopropane ring opening, but equally could derive from the lower activation energy of the concerted mechanism. The latter view is favoured by the observation that Hanafusa's acid (1) is structurally incapable of isomerising to a βγ-unsaturated acid and cannot decarboxylate by the stepwise mechanism (3).

We decided therefore to examine some other cyclopropylacetic acids in an attempt to elucidate their mechanisms of pyrolysis. We report below experiments which define for the first time the concerted mechanism (2) and (3). We will report later on the incursion of the stepwise mechanism.

EXPERIMENTAL

Preparation of the Acids.—The acids were prepared by a Simmons–Smith[5] reaction on the previously described βγ-unsaturated esters.[6] In general it was necessary to use a 2—5 fold excess of the Simmons–Smith reagent to maximise yields. The following preparation is typical. Zinc–copper couple was prepared in two stages. Zinc powder was stirred rapidly with excess of 6M-hydrochloric acid for 5 min. The metal was filtered at the pump, washed successively with water, ethanol, acetone, and diethyl ether and dried in a vacuum oven. This metal (65.4 g, 1 mol) was then stirred into water (100 ml) and a solution of AnalaR copper sulphate (2.5 g, 0.01 mol) in water (50 ml) rapidly added. The solid material was then quickly filtered at the pump and washed and dried as above.

Ethyl 2,2-dimethylbut-3-enoate (20.2 g, 0.14 mol), di-iodomethane (74 g, 0.28 mol), zinc–copper couple (19.6 g, 0.3 mol), and sodium dried ether (150 ml) were stirred and refluxed under nitrogen for 72 h, when further portions of di-iodomethane (37 g, 0.14 mol) and zinc–copper couple (9.8 g, 0.15 mol) were added and reaction was continued for a further 24 h. After cooling the mixture was filtered, and the filtrate was cautiously acidified with 3M-hydrochloric acid. The ester was isolated by ether extraction, the neutral ether layer being washed with aqueous sodium thiosulphate to remove iodine. Removal of the ether gave ethyl 2-methyl-2-cyclopropylpropanoate as an oil, b.p. 79—80° at 21 mmHg (17 g, 0.11 mol, 75%), having no absorption at 1 640 cm^{-1} but a new absorption at 1 020 cm^{-1}. The ester (4.5 g, 0.03 mol) was hydrolysed by refluxing for 18 h with potassium hydroxide (10 g) in 50% aqueous ethanol (20 ml). Water (50 ml) was added to the cooled solution and the ethanol was removed by evacuation. The usual ether extraction and decolourisation with animal charcoal gave *2-methyl-2-cyclopropylpropanoic acid* (I) (3.0 g, 0.023 mol, 77%) as crystals, m.p. 35° (from pentane at —20°) (Found: C, 65.8; H, 9.6. $C_8H_{12}O_2$ requires C, 65.6; H, 9.45%).

2-Methyl-2-(1-methylcyclopropyl)propanoic acid (II) had m.p. 64° (Found: C, 67.7; H, 10.1. $C_8H_{14}O_2$ requires C, 67.55; H, 9.9%). *(1-Methylcyclopropyl)ethanoic acid* (III) had b.p. 64—66° at 0.5 mmHg (Found: C, 62.9; H, 8.9. $C_6H_{11}O_2$ requires C, 63.1; H, 8.8%).

2-Methyl-2-(1-ethyl-2-methylcyclopropyl)propanoic acid (IV). The Simmons–Smith reaction on ethyl 2,2-dimethyl-3-ethylpent-3-enoate could not be made to proceed beyond 80%. The two esters showed no obvious difference in hydrolysis rate and were hydrolysed together to the mixed acids. These were dropped in pentane solution under

nitrogen through a vertical packed column (670 K, contact time *ca.* 5 s) which gave a product containing only 1% of the unsaturated acid. Repetition of this pyrolysis gave pure (IV), m.p. 45—51°. Several recrystallisations of this material gave a solid, m.p. 57—58°, having a simple ^{13}C n.m.r. spectrum, and a small quantity of an oil, m.p. *ca.* 0°, whose ^{13}C n.m.r. spectrum showed shadows with 67% the intensity of the main peaks. It was assumed that the solid was a pure isomer while the oil was a mixture of geometric isomers. Unfortunately assignment of configuration to a single isomer is not possible (Found: C, 70.5; H, 10.7. $C_{10}H_{18}O_2$ requires C, 70.55; H, 10.65%).

2-Methyl-2-(bicyclo[3.1.0]hex-1-yl)propanoic acid (V) had m.p. 68—69° (Found: C, 71.2; H, 9.6. $C_{10}H_{16}O_2$ requires C, 71.4; H, 9.6%). 2-Methyl-2-(bicyclo[4.1.0]hept-1-yl)-propanoic acid (VI), had m.p. 53—54° (Found: C, 72.75; H, 9.8. $C_{11}H_{18}O_2$ requires C, 72.5; H, 9.95%). 2-Methyl-2-(bicyclo[5.1.0]oct-1-yl)propanoic acid (VII) had m.p. 80—81° (Found: C, 73.5; H, 10.35. $C_{12}H_{20}O_2$ requires C, 73.45; H, 10.25%). 2-Methyl-2-(bicyclo[6.1.0]non-1-yl)-propanoic acid (VIII) had m.p. 69—71° (Found: C, 74.05; H, 10.45. $C_{13}H_{22}O_2$ requires C, 72.25; H, 10.55%).

All these acids had i.r. and ^1H n.m.r. spectra in accord with expectation and were obtained in 30—77% yields from the preceding unsaturated ester.

Products and Stoicheiometry.—All acids gave a quantitative yield of carbon dioxide, within experimental error. Acid (I), examined in an evacuated sealed tube gave 89% 2-methylpent-2-ene and 6% 2-methylpent-1-ene (the former slowly isomerises to the latter at this temperature, 350°). The remaining acids were examined by dropping them in solution through a 30 × 5 cm glass bead packed column at 450° under nitrogen. The olefins were separated by preparative g.l.c. and were identified either by comparison with authentic samples (g.l.c.) or when new compounds (italics) by ^1H n.m.r., ^{13}C n.m.r., and precise mass measurement. The yields quoted are probably a measure of trapping efficiency, the actual yields being larger.

Acid (II) gave 2,3-dimethylpent-2-ene (95%). Acid (III) gave 2-methylbut-1-ene (96%). Acid (IV) gave 2,4-*dimethyl-3-ethylpent-2-ene* and 2-*methyl-3-ethylhex-2-ene* (94%). Acid (V) gave 2-*methylisopropylidenecyclopentane* and isopropylidenecyclohexane (96%). Acid (VI) gave 2-*methylisopropylidenecyclohexane* and isopropylidenecyclo-heptane (96%). Acid (VII) gave *methylisopropylidene-cycloheptane* and isopropylidenecyclo-octane (98%). Acid (VIII) gave 2-*methylisopropylidenecyclo-octane* and (probably) isopropylidenecyclononane (95%).

Kinetics.—Kinetic runs in a series of evacuated sealed tubes gave erratic results suggestive of surface activity. Kinetic runs were performed in our flow apparatus and the reactions shown to be of the first order by the test described earlier.[7] Only acid (I) was sufficiently volatile for convenient g.l.c. analysis, and the kinetics of decomposition of this acid were followed by observing disappearance of starting material in the usual fashion. The decomposition of the remaining acids was more conveniently followed by observing the appearance of carbon dioxide. If C_T is the ratio of carbon dioxide to standard at a given temperature, and C_{100} is the ratio calculated for 100% reaction (obtained by prior calibration), then $a/a_0 = 1 - C_T/C_{100}$ and the activation parameters were obtained from least squares plots of $\log(-\log a/a_0)$ *versus* $1/T$ after the method of Kooyman.[8] The activation parameters are given in Table 1.

TABLE 1

Activation parameters for the gas-phase pyrolysis of some cyclopropylacetic acids (690—740 K)

Acid	$\Delta H^\ddagger$/kJ mol^{-1}	$\Delta S^\ddagger$/J K^{-1} mol^{-1}	Gradient of confidence ellipse α/K [8]
(I)	185.8 ± 2.9	−45.5 ± 3.7	747.7
(II)	175.8 ± 4.2	−40.4 ± 6.7	747.9
(III)	170.9 ± 10.9	−54.5 ± 14.4	770.9
(IV)	176.2 ± 5.2	−30.0 ± 7.1	737.0
(V)	168.3 ± 6.7	−50.7 ± 9.2	717.8
(VI)	149.9 ± 7.1	−72.5 ± 10.0	710.3
(VII)	144.9 ± 6.3	−77.4 ± 8.4	708.3
(VIII)	142.2 ± 9.2	−79.5 ± 12.6	733.8

The rates of reaction were unaffected by the addition of 500 mole % of cyclohexene, but the use of a packed flow tube suggested incursion of up to 5% of a surface reaction. Typical results are shown in Table 2.

TABLE 2

Tests for heterogeneity in the pyrolysis of cyclopropylacetic acids (725 K)

Acid	$10^3 k$/s^{-1}	A	B	C
(II)	26.3 ± 1.5	28.0	38.3	3.2
(V)	25.3 ± 1.0	26.5	43.0	5.0
(VIII)	61.5 ± 1.9	60.1	79.6	2.1

A, $10^3 k$/s^{-1} in presence of 500 mole % cyclohexane; B, $10^3 k$/s^{-1} in packed tube; C, heterogeneous component in normal runs estimated from surface : volume ratios.

TABLE 3

Rate constants for the pyrolysis of acids (I)—(VIII) at 725 K

Acid	$10^3 k$/s^{-1}	$10^3 k_a$/s^{-1}	$10^3 k_b$/s^{-1}	$10^3 k_c$/s^{-1}
(I)	2.62 ± 0.10	1.31	1.31	<0.05
(II)	26.3 ± 1.5	13.2	13.2	0
(III)	82.4 ± 3.5	44.9	37.5	0
(IV)	10.5 ± 1.0	5.25	5.25	0
(V)	25.3 ± 1.0	15.6	9.7	0
(VI)	39.6 ± 1.6	30.9	8.7	0
(VII)	50.9 ± 2.1	45.6	5.3	0
(VIII)	61.5 ± 1.9	56.7	4.8	0

Rate constants calculated from the Arrhenius data of Table 1 are shown in Table 3. Where more than one product resulted, the overall rate constant is divided *pro rata*. The definitions of k_a, k_b, and k_c are given in the Discussion section.

Deuteriated acids were prepared by the reported method [9] and their olefins isolated as described above.

DISCUSSION

The pyrolyses of acids (I)—(VIII) are of the first order, unaffected by the radical trap cyclohexene and >95%

(I)   (II)   (III)   (IV)

$(CH_2)_n CO_2H$

(V)   n = 3
(VI) n = 4
(VII) n = 5
(VIII) n = 6
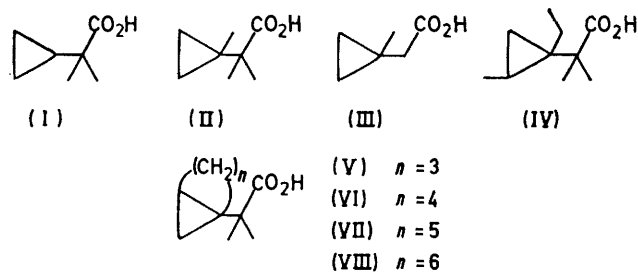
homogeneous. The reactions are thus almost certainly unimolecular. It is noteworthy that the reactions led to

products formed almost exclusively by ring opening of the two alternate $\beta\gamma$-positions in the ring (a and b).
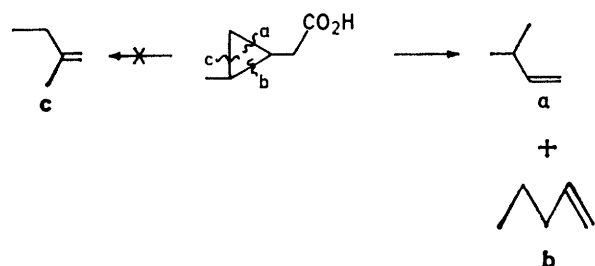
Only acid (I) in this series is capable of isomerising following ring scission at c, the other acids having no β-hydrogen atom for transfer after the bond breaking. For acid (I), however, ring scission solely at a and b follows automatically as a consequence of the concerted mechanism (1) and (2) but is difficult to explain in terms of the stepwise mechanism (3).

The activation parameters of Table 1 also favour the concerted mechanism. The average entropy of activation for the four monocyclic acids (I)—(IV) is -42.6 J K^{-1} mol^{-1}. These values are similar to those of other multicentre reactions which involve the loss of three internal rotations on going to the transition state,[10] and are far removed from the values that have been experimentally determined for the rearrangements of cyclopropanes to olefins.[11] The closest analogy comes from our own work, the decomposition of the identically substituted $\beta\gamma$-unsaturated acids having an average entropy of activation of -43.5 J K^{-1} mol^{-1}.[6,12]

The entropies of activation for the bicyclic acids (V)—(VII) are less persuasively explicable as being diagnostic of a multicentre pathway. The average value (-70 J K^{-1} mol^{-1}) cannot be correlated with the loss of only three rotations on going to the transition state. Very similar data have been reported [6] and criticised [13] for the corresponding olefinic acids. It seems possible that in these increasingly crowded acids either the 2-methyl groups or some ring fluxions become hindered on going to the transition state, adding to the loss of entropy.

The enthalpies of activation of Table 1 also favour the concerted mechanism as they are ca. 90—110 kJ mol^{-1} below those measured for the isomerisation of cyclopropanes to olefins.[11]

The rate data of Table 3 are compared with the closest available cyclopropanes and the olefinic counterparts in the Scheme (725 K). It is difficult to estimate the effect to be expected of an electron-withdrawing β-carboxy group on the rate of ring opening of cyclopropane. However, 2,2,2-trifluoroethylcyclopropane is pyrolysed ca. 10 times slower than ethylcyclopropane at 725 K,[17] suggesting the hydrocarbons of the Scheme represent maximum rates. This being so, the 40—300-fold difference in rate is difficult to reconcile with the stepwise mechanism involving an initial ring opening.

The concerted mechanism might show similarities with $\beta\gamma$-unsaturated acids in a structure–reactivity order.

Such a comparison is not likely to be precise as the $\beta\gamma$-unsaturated acids are about three orders of magnitude more reactive at the same temperature (Scheme) and to compare the two series reacting at similar rates would involve a temperature difference of $>200°$. Nevertheless certain similarities emerge. α-Substituents enhance the rate of decomposition ca. 2.6-fold, while β-substituents do so by 10-fold or more; γ-substituents reduce it.[6] By contrast β-substitution of a cyclopropane ring has little effect on its rate of ring opening.[11]
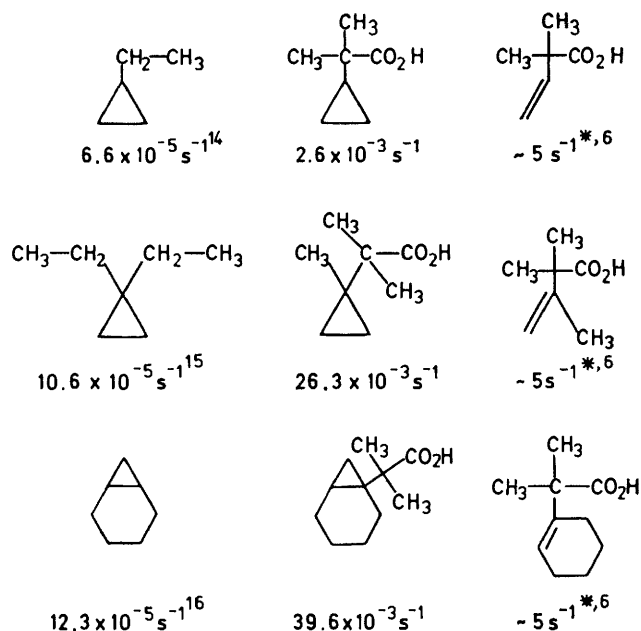
SCHEME * These figures are extrapolated from 500 K and are therefore imprecise

The deuteriated acids were examined kinetically and their product olefins examined. The concerted mechanism (1) and (2) should exhibit a deuterium kinetic isotope effect. In the stepwise mechanism (3) the carboxy hydrogen atom is transferred after the rate-determining step and there should be no kinetic isotope effect. Experiment showed that acid (II) had k_H/k_D 1.9 $\pm$ 0.25 at 725 K. At this temperature the maximum value is 2.6 [given by k_H/k_D $\exp(5852/RT)$ [18,19]]. The measured isotope effect is therefore 73% of maximum and is indicative of the concerted mechanism (1) and (2).

The position of deuterium label in the olefins from pyrolysis of carboxy-^{2}H labelled acids (I), (III), (VI), and (VII) was examined by ^{1}H n.m.r. and noise decoupled ^{13}C n.m.r. spectroscopy. With acids (I) and (III) a single product was isolated [reaction (4)], but with acids (VI) and (VII) only the major isomer could be obtained in sufficient quantity for n.m.r. analysis [reaction (5)]. The position of label in the minor product would have been more difficult of assignment, e.g. reaction (6).

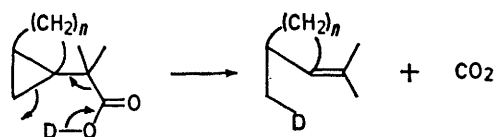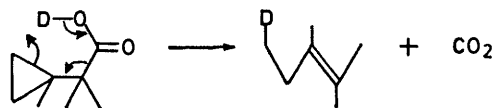In conclusion, all the evidence described in this paper gives unequivocal support to the concerted mechanism,

there being no indication at all of the stepwise route. It should be noted, however, that up to 10% incursion of
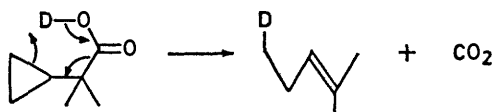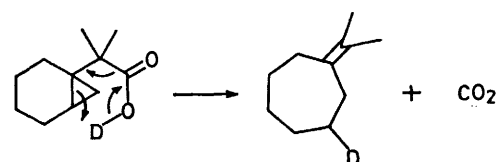

(4)

(5)

(VI) $n = 4$
(VII) $n = 5$

(6)

the stepwise route might have gone undetected and we shall return to this point in a later paper.

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