Studies in Decarboxylation. Part 10.[1] Effect of β-Substituents on the Rate of Gas-phase Decarboxylation of βγ-Unsaturated Acids

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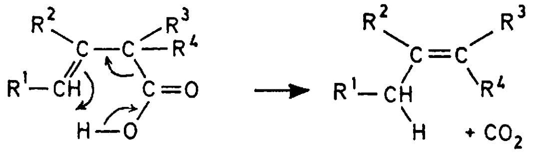
The large rate enhancements in the gas-phase decarboxylation of βγ-unsaturated acids resulting from substitution of the β-carbon atom are shown to be derived from increased nucleophilicity of the γ-carbon atom. This being so, the carboxylic hydrogen atom must be transferred as an electrophile, and the direction of the other electron movements is thereby implied.

In Part 4[2] we described the synthesis of a group of βγ-unsaturated acids with various alkyl substituents at the α-, β-, and γ-carbon atoms, and an examination of the effect of these substituents on the rate of gas-phase decarboxylation (Scheme 1). In summary: (i) a γ-methyl group ($R^1 = Me$) reduced the rate of decarboxylation in comparison with the unsubstituted acid ($R^1 = H$) by a factor of *ca.* 7. During decarboxylation the double bond migrates to the adjacent position and this process is less thermodynamically favourable in the substituted than in the unsubstituted acid; it was argued that the rates would be similarly related. (ii) Two α-methyl groups ($R^3 = R^4 = Me$) on the α-carbon atom accelerated the reaction, and this was taken to be an indication of greater product stability being reflected in the transition state. (iii) On the basis of analyses (i) and (ii) it was expected that a β-alkyl group would have little effect on the rate of decarboxylation, as it would have interacted equally with the double bond at either the origin or the terminus of migration. In fact a large increase in rate was observed and was ascribed to a steric origin (the interaction of R^2 with the isobutyric acid was identified as the major source of strain). The quaternary C-2 becomes trigonal after loss of carbon dioxide, with a corresponding relief of congestion. It was therefore argued that the high rate of reaction resulted from destabilization of the starting material.



Scheme 1

Two tests of this explanation can be made. In the first the possibility of strain affecting the rate of reaction can be examined by incorporation of the double bond in rings of various sizes. This test was applied in Part 4[2] and the rate of decarboxylation was indeed found to vary with ring size.

The second test is more direct and would examine the effect on rate of decarboxylation of reduction in the congestion at C-2 by removal of one or both of its methyl groups. All the acids studied in Part 4 contained this pair of α-methyl groups to prevent αβ–βγ thermal isomerization,[3] which could have occurred with our sealed tube technique.

We have recently shown that our flow apparatus[4] does not cause isomerization of βγ-unsaturated acids,[5] and this paper describes our return to the second test of our explanation.

RESULTS AND DISCUSSION

Table 1 shows the rates of pyrolysis of four acids at 500 K, the standard temperature we have used for comparisons in this series of papers. The sequence (1) ⟶ (2) ⟶ (4) was referred to in the Introduction, the increasing rate constants being attributed to increased congestion.[2] We have now examined 3-methylbut-3-enoic acid (3) using our flow apparatus;[4] it exhibits $\Delta H^{\ddagger} = 144.8$ kJ mol^{-1} and $\Delta S^{\ddagger} = -45.9$ J K^{-1} mol^{-1}. All four acids therefore have approximately the same value for $\Delta S^{\ddagger}$, a value characteristic of a six-centre concerted transition state. The relative rates of reaction are therefore controlled by the enthalpy term, which is consistent with increasing relief of strain in going to the transition state in the sequence (1) ⟶ (2) ⟶ (4).

Table 1

Rates (s^{-1}) and relative rates (italics) of pyrolysis of some unsaturated acids at 500 K

$CH_2{:}CH{\cdot}CH_2{\cdot}CO_2H$	$CH_2{:}CH{\cdot}CMe_2{\cdot}CO_2H$
(1)	(2)
1.50×10^{-6}; *1*	1.38×10^{-5}; *9.2*
$CH_2{:}CMe{\cdot}CH_2{\cdot}CO_2H$	$CH_2{:}CMe{\cdot}CMe_2{\cdot}CO_2H$
(3)	(4)
3.05×10^{-5}; *20.3*	2.94×10^{-4}; *196*

The rate measured for the new acid (3) shows this explanation to be incorrect, however. Comparison of the relative rates for (1) and (2) with those for (3) and (4) indicates that the introduction of two geminal methyl groups has the same effect in either case. Since (2) can by no means be considered sterically crowded, it follows that (4) cannot be either. Comparison of (1) with (3) shows the effect of introducing a β-methyl group into an uncrowded system. The almost identical value for comparison of (2) and (4) again implies an absence of kinetically significant crowding in (4).

The increase in the rate of decarboxylation caused by introduction of a β-methyl group must therefore be due to an electronic effect. Inductive stabilization of a zwitterion (B) would account for the acceleration, but

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[1] Part 9, D. B. Bigley and R. H. Weatherhead, *J.C.S. Perkin II*, 1976, 704.

[2] D. B. Bigley and R. W. May, *J. Chem. Soc.* (*B*), 1967, 557.

[3] R. T. Arnold, O. C. Elmer, and R. M. Dodson, *J. Amer. Chem. Soc.*, 1950, **72**, 4359.

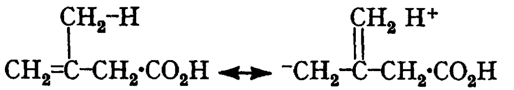
[4] D. B. Bigley and C. M. Wren, *J.C.S. Perkin II*, 1972, 926.

[5] D. B. Bigley and R. H. Weatherhead, *J.C.S. Perkin II*, 1976, 592.

such a mechanism has already been eliminated on other grounds.[6]

$$\underset{\text{(A)}}{CH_2{:}CMe{\cdot}CH_2{\cdot}CO_2H} \rightleftharpoons \underset{\text{(B)}}{CH_3{\cdot}{}^{+}CMe{\cdot}CH_2{\cdot}CO_2^{-}} \longrightarrow \text{products}$$

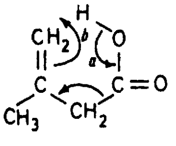
One is forced to conclude that the effect of the β-methyl group is to enhance the nucleophilicity of the γ-carbon atom [see (C)], resulting in electrophilic attack on it.



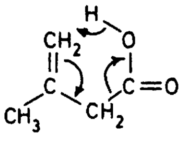
$$CH_2{=}\overset{\overset{CH_2-H}{|}}{C}{-}CH_2{\cdot}CO_2H \longleftrightarrow {}^{-}CH_2{-}\overset{\overset{CH_2\ H^+}{\|}}{C}{-}CH_2{\cdot}CO_2H$$

(C)

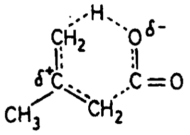
The transferred hydrogen atom must therefore be positive with respect to the γ-carbon atom and is more likely to have proton character than the hydride nature once considered by Swain for the closely related β-oxo-acids.[7] In such terms formulation (D) (with electron movement *a* preceding *b*) is to be preferred to (E), with its implied 1,5-hydride shift. An alternative but equivalent description would be as a concerted but *dipolar* transition state (F).



(D)



(E)



(F)

Table 2 shows the rate constants and relative rates for the first two acids of Table 1 at 456.4 K compared with those for the phenyl-substituted analogues of (3) and (4). 3-Phenylbut-3-enoic acid (5) proved to be the most reactive βγ-unsaturated acid we have so far encountered, and the phenyl ring renders it less volatile than its aliphatic counterpart (3).

TABLE 2

Rates (s^{-1}) and relative rates (italics) of pyrolysis of some unsaturated acids at 456.4 K

$CH_2{:}CH{\cdot}CH_2{\cdot}CO_2H$	$CH_2{:}CH{\cdot}CMe_2{\cdot}CO_2H$
(1)	(2)
3.18×10^{-8}; *1*	4.09×10^{-7}; *12.9*
$CH_2{:}CPh{\cdot}CH_2{\cdot}CO_2H$	$CH_2{:}CPh{\cdot}CMe_2{\cdot}CO_2H$
(5)	(6)
2.72×10^{-4}; *8 550*	3.79×10^{-5}; *1 190*

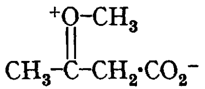
Our flow apparatus is not suitable for compounds with these properties as, depending on temperature, they are either not completely volatilized or fully decomposed. We had therefore to revert to the evacuated sealed tube technique [8] and are correspondingly less certain that no isomerization occurred. We were not able to detect any β-methylcinnamic acid at any stage, but it would be prudent to regard the rate constant quoted for (5) as a minimum. Further, we confined our investigations to a single temperature.

There are two principal features to Table 2. The much greater spread of rates is real but is in part due to the temperature of reaction. Thus at this temperature the acid (4) (Table 1) would have a relative rate of 400, almost twice that quoted for 500 K. Secondly, the order of relative rates of (5) and (6) is the reverse of that for (3) and (4).

In Part 6 we noted that acids of the type (6) have little conjugation between the benzene ring and the double bond, at least as evidenced by their u.v. spectra.[6] The large 3-phenyl group interacts with the substituents on C-2, but this repulsion is minimized when its plane is at right angles to the π-system of the olefin. On the other hand the acid (5) has $\lambda_{max.}$ 243 nm (log ε 4.01) [*cf.* α-methylstyrene, $\lambda_{max.}$ 244 nm (log ε = 4.09) [9]], showing there to be a large interaction between the π-systems of the double bond and the benzene ring.

These two aromatic acids now fall into place with our rationalization of Table 1. The γ-carbon atom of the more conjugated acid (5) will be more nucleophilic than that of the aliphatic acid (3), since conjugative effects are usually larger than inductive/hyperconjugative effects. The reduced conjugation of acid (6) will make it less reactive than (5), but it should be more reactive than (4) since the inductive effect of the phenyl group is still available in addition to any residual conjugation.

A useful test of this theory of enhanced nucleophilicity of the γ-carbon atom would be an examination of the properties of 3-methoxybut-3-enoic acid. This acid should possess a highly nucleophilic terminal methylene group, but unfortunately it has never been described. It seems possible that it would not be stable, but would decompose or rearrange *via* a zwitterion (G), and it is noteworthy in this connection that its αβ-unsaturated isomer, 3-methoxycrotonic acid, is decarboxylated rapidly at 180 °C.[10] αβ-Unsaturated acids are usually stable at this temperature, and the unusual behaviour of 3-methoxycrotonic acid could be due to its forming the *same* zwitterion, although its α-carbon atom should be less nucleophilic than the γ-carbon of its βγ-isomer.



$$CH_3{-}\overset{\overset{{}^{+}O-CH_3}{\|}}{C}{-}CH_2{\cdot}CO_2^{-}$$

(G)

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[6] D. B. Bigley and J. C. Thurman, *J. Chem. Soc.* (*B*), 1968, 436.

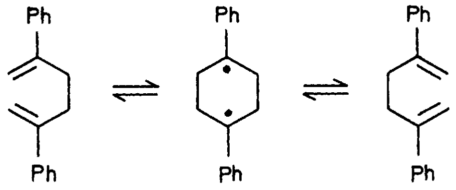
[7] C. G. Swain, R. F. W. Bader, R. M. Esteve, and R. N. Griffin, *J. Amer. Chem. Soc.*, 1961, **83**, 1951.

[8] D. B. Bigley, *J. Chem. Soc.*, 1964, 3897.

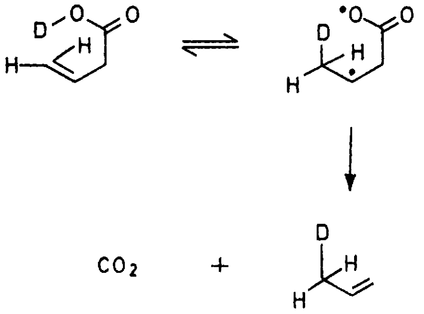
[9] E. A. Brande and C. J. Timmons, *J. Chem. Soc.*, 1950, 2000.

[10] W. J. leNoble and P. J. Crean, *J. Org. Chem.*, 1962, **27**, 3875.

Dewar has reported rate enhancements similar to those discussed above in the Cope rearrangement, and has proposed a diradical intermediate [11] (Scheme 2). We do not wish to criticize this proposal, but comment that the acid/base mechanism could also be applied here. On the other hand Dewar's diradical intermediate is unacceptable in the present case as it predicts scrambling of isotopic label from the carboxy-group; this is not observed [6] (Scheme 3). There remains the question of the possible effect on rate of decarboxylation of strain on the double bond. In Part 4 we described compounds with the double bond in rings of five to seven carbon atoms, and we have now added 2-(cyclo-oct-1-enyl)-2-methylpropionic acid to the series, as shown in Table 3. The first-order rate constants at 500 K are all large, as expected of acids bearing β-alkyl groups. The right-hand column shows these rates divided by that of the acylic analogue. According to this quotient, incorporation of the double bond in a ring can either accelerate or decelerate the reaction, the overall range being five-fold. While this range is not large, α- or γ-methylation has an effect of similar magnitude.[2] We conclude, since the electronic environment of all the cyclic acids is identical, that the variation of rate must result from strain, although we do not wish to specify its precise origin.[12]



Scheme 2



Scheme 3

Table 3

First-order rate constants (k) for the gas-phase decarboxylation of some cyclic acids at 500 K

$\overline{[CH_2]_n\cdot CH{:}C}\cdot CMe_2\cdot CO_2H$	k/s^{-1}	$k/k(MeCH{:}CEt\cdot CMe_2\cdot CO_2H)$
$n = 3$ [a]	8.04×10^{-5}	0.90
$n = 4$ [a]	3.31×10^{-5}	0.38
$n = 5$ [a]	1.12×10^{-4}	1.3
$n = 6$ [b]	1.66×10^{-4}	1.9

[a] Ref. 2. [b] Present work.

EXPERIMENTAL

Preparation of Acids.—The preparation of 3-methylbut-3-enoic acid (3) has been said to require copper apparatus and a large scale.[13] We were successful with a 0.75 mol preparation in glass apparatus. The acid had b.p. 68—70° at 5 mmHg, n_D^{20} 1.430 8 (lit. values identical [13]), and solidified just below room temperature. 3-Phenylbut-3-enoic acid (5) was prepared by the method of Maercker and Weber [14] and had m.p. 49—49.5° (lit.,[14] 48—49.5°). 2-*(Cyclo-oct-*1-*enyl)*-2-*methylpropionic acid* was prepared by the route described in Part 4.[15] The hydroxy-ester (b.p. 129—134° at 10 mmHg, n_D^{20} 1.475 3) resulting from a Reformatskii reaction between cyclo-octanone and ethyl 2-bromoisobutyrate was dehydrated over phosphorus pentaoxide. Hydrolysis of the unsaturated ester (b.p. 106—110° at 4 mmHg) gave the desired acid, m.p. 83.5—84.0° (Found: C, 73.45; H, 9.95. $C_{12}H_{20}O_2$ requires C, 73.45; H, 10.2%).

Kinetics.—3-Methylbut-3-enoic acid was studied in the previously described flow system [5] and gave quantitative yields of carbon dioxide and isobutene. The other two acids were studied by using break-seal tubes and both gave >99% yields of carbon dioxide. In addition 3-phenylbut-3-enoic acid gave α-methylstyrene, and 2-(cyclo-oct-1-enyl)-2-methylpropionic acid gave pure isopropenylcyclo-octane.[12]

We thank Professor R. F. Hudson for discussions and the S.R.C. for studentships (to R. H. W. and R. W. M.).

[6/1496 *Received, 2nd August*, 1976]

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[11] M. J. S. Dewar and L. E. Wade, *J. Amer. Chem. Soc.*, 1973, **95**, 290.

[12] D. B. Bigley and R. W. May, *J. Chem. Soc. (B)*, 1970, 1761.

[13] R. B. Wagner, *J. Amer. Chem. Soc.*, 1949, **71**, 3214.

[14] A. Maercker and K. Weber, *Annalen*, 1972, **756**, 20.

[15] D. B. Bigley and J. C. Thurman, *J. Chem. Soc.*, 1965, 6202.