Thermal Isomerization of Alkylcyclopropenes

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Summary Kinetic study of the thermal isomerization of four methyl-substituted cyclopropenes indicates that increased substitution causes a marked increase in thermal stability.

THE effect of increased alkyl substitution on the kinetics of the thermal decomposition of small-ring hydrocarbons is a useful probe into the mechanisms of these reactions. It has been shown[1] that on alkyl substitution the rate of isomerization of cyclopropanes increases while cyclobutanes are little affected, and cyclobutenes are sensitive to the position of the substituent. We report data on the kinetics and chemistry of the thermal isomerization of four methyl-substituted cyclopropenes.

The compounds studied, products observed, and rate data are listed in the Table. These data were obtained in the gas phase with the usual controls to ensure that the reactions were homogenous and kinetically of first-order. They are almost certainly unimolecular.

One or possibly two isomerization modes prevail in the compounds studied here and those reported earlier[2] and lead to alkynes or conjugated dienes. When three methyl groups were introduced into the ring, a sharp increase in

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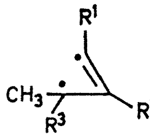
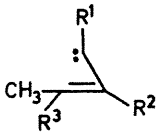
Cyclopropene	Reaction temperature	Products[a] 1,3-diene		alkyne		Activation[c] energy kcal mol^{-1}	Log A[c] factor	$k \times 10^4$ at 500 K
(IVa)	471—502	(V)	10%	(XI)	90%	37·60 ± 1·20	13·5 ± 0·5	10·0
(IVb)	472—505	(VI)	10%	(XII)	90%	36·60 ± 0·85	13·0 ± 0·4	8·9
(IVc)	491—518	(VII) (VIII)	71% 21%	[b]		39·00 ± 1·35	13·4 ± 0·6	1·5
(IVd)	533—571	(IX) *cis* *trans* (X)	5% 85% 10%			39·97 ± 2·00	12·5 ± 0·8	0·1

[a] Product compositions varied within ±10% over the temperature ranges used. Since analyses for individual compounds were uncertain to at least ±5%, rate parameters for each product were not determined. [b] 5 minor products (< 5% each) were also formed. [c] Uncertainties are 95% confidence limits.

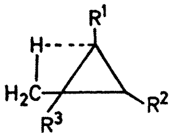
the activation energy for the isomerization was observed, and the major process changed abruptly from alkyne formation to diene production.



(I)



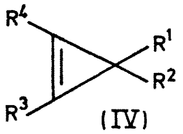
(II)



(III)

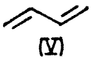
(I), (II), and (III) are three possible intermediates in the thermal isomerization of a typical cyclopropene. Since the tendency of intermediates such as (II) (generated from the tosylhydrazones) to close[3] and the thermal stability of the corresponding cyclopropenes observed in this study appear to be unrelated, the intermediate (II) probably has a limited role in the thermal isomerization of cyclopropenes and (I) may be selected as the precursor to alkyne formation (*cf.* the parallel reaction in cyclopropanes).[1] Intermediate (III) suggests a concerted H-migration and explains the formation of a diene with retention of the stereochemistry as shown by Stechl[4] and confirmed in this work in the case of tetramethylcyclopropene. However, it is not possible to generalize from this single instance and say H-migration need always be concerted.

I thank Mr. A. R. Taranko for technical assistance.

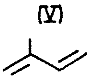


(IV)

a; R^1 = Me, R^2 = R^3 = R^4 = H
b; R^1 = R^2 = Me; R^3 = R^4 = H
c; R^1 = R^2 = R^3 = Me, R^4 = H
d; R^1 = R^2 = R^3 = R^4 = Me

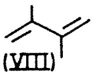


(V)

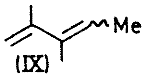


(VI)

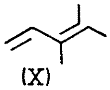
(VII)



(VIII)



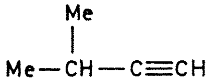
(IX)



(X)

Me—CH$_2$—C≡CH

(XI)



$$\mathrm{Me{-}\overset{\displaystyle Me}{\overset{|}{C}H}{-}C{\equiv}CH}$$

(XII)

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[1] For a review of work published up to 1965 on the pyrolysis of small-ring hydrocarbons see H. M. Frey, *Adv. Phys. Org. Chem.*, 1965, **4**, 147.

[2] R. Srinivasan, *J. Amer. Chem. Soc.*, 1969, **91**, 6250.

[3] G. L. Closs, L. E. Closs, and W. A. Böll, *J. Amer. Chem. Soc.*, 1963, **85**, 3796.

[4] H.-H. Stechl, *Chem. Ber.*, 1964, **97**, 2681.