Rearrangements of Bicyclic Cyclopropylcarbenes. Temperature Dependence of Product Ratios

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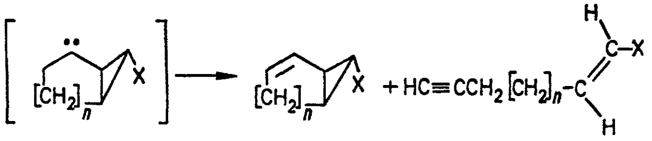
Summary A substituent effect on the activation energy for the cyclopropylcarbene → olefin + acetylene ring cleavage in two bicyclic systems implies charge transfer from cyclopropane at the transition state.

CARBENE reactions are generally assumed to have very small (or non-existent) activation energies. However, to our knowledge, the activation parameters of a carbene reaction have never been measured, and very few studies of differences in activation parameters for competitive carbene reactions are reported.[1]

We have observed that the product ratios (**2**) : (**3**) from the bicyclic cyclopropylcarbenes (**1**; $n = 1$ or 2) do vary with temperature when $X = CO_2Et$ but do not (within the limits of detection) when $X = H$. We interpret these results in terms of a substituent effect on the activation energy for the ring cleavage reaction leading to (**3**).[2]

The Table summarizes the distributions of products from the four carbenes of general structure (**1**). Carbenes were generated by thermolysis of the appropriate dry tosylhydrazone sodium salts in diglyme or triglyme.


(1) (2) (3)

Products (**2**) and (**3**) [as well as the undetected *endo*-(**2**) and *cis*-(**3**)] were shown to be stable to the reaction conditions at all temperatures, except that (**3**; $X = H$) is partially isomerized to the corresponding allene, $H_2C{=}C{=}CH[CH_2]_nCH{=}CH_2$. This isomerization, also reported by Freeman and Kuper,[3] presumably accounts for the presence of allenes in the product mixtures from (**1**; $X = H$).

Arrhenius plots of log (k_2/k_3) *vs.* $1/T$ for the temperature-dependent carbene reactions ($X = CO_2Et$) give the differences in activation energies $E_3 - E_2 = \Delta\Delta H^{\ddagger} = 8{\cdot}0 \pm 2{\cdot}0$ kJ/mol ($1{\cdot}9 \pm 0{\cdot}5$ kcal/mol) for both the bicyclo[3,1,0]- and the bicyclo[4,1,0]-systems.† The corresponding activation energy (or activation enthalpy) difference for the temperature-independent cases ($X = H$) must be $\leqslant 2$ kJ/mol (0·5 kcal/mol).‡

It seems unlikely that *exo*-substitution of CO_2Et for H would affect the hydrogen migration, so apparently the electronegative ester substituent raises the activation energy for ring cleavage by 4—10 kJ/mol (1—2 kcal/mol). This suggests that charge donation from cyclopropane to the empty *p*-type orbital at the carbene centre is important at the transition state for ring cleavage.§ Such a picture of the ring cleavage process is not unreasonable in view of the propensity of cyclopropane to act as a donor,[4] the similarities between these cyclopropylcarbenes and cyclopropylcarbinyl cations,¶ and the electronic redistribution involved in going from carbene to ring-cleaved product (**3**). Some charge transfer is also expected in the ground state of these cyclopropylcarbenes, according to calculations by Hoffmann, *et al.*[5]

TABLE

Ratios of products from the carbenes (**1**)

			Products[a]	
n	X	Temperature (t/°C)	(**2**)	(**3**)[c]
1	H	120—200	16[b,d]	84[b,d]
1	CO_2Et	200	85	15
		150	88	12
		120	89	11
		90	91	9
2	H	120—200	84[b]	16[b]
2	CO_2Et	200	55	45
		150	60	40
		120	65	35
		90	69	31

[a] Ratios by g.l.c. (±1%); overall yields at 150 and 200 °C were >85%. [b] Temperature-independent ratios. [c] Actually, (**3**) + allenes. [d] Same product ratio reported in ref. **3**, in which products were distilled out of reaction mixture.

It might be noted that detailed mechanistic arguments based on carbene product ratios at a single temperature are subject to question in light of the temperature effects reported here.

The stereospecificity** of the ring cleavage ($X = CO_2Et$) suggests, but does not require, a concerted reaction[6] from singlet carbene and will be discussed elsewhere in conjunction with the *endo*-CO_2Et results.

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† Rate constant ratios $k_2 : k_3$ equal product ratios; subscript numeral refers to product being formed.

‡ However, it is possible (according to simple RRKM calculations) that these carbenes ($X = H$), formed with excess vibrational energy in the loss of N_2 from intermediate diazo-compounds, are rearranging at rates competitive with collisional deactivation; if so, the product ratio would be insensitive to small differences in activation energy. For MINDO/2 calculations on the hydrogen migration process, see N. Bodor and M. J. S. Dewar, *J. Amer. Chem. Soc.*, 1972, **94**, 9103.

§ The most stable configuration of these cyclopropylcarbenes is calculated[5] to be σ^2p^0 with geometry analogous to the stable 'bisected' conformation of the cyclopropylcarbinyl cation.

¶ A marked dependence of the product ratio ($n = 1$, $X = H$; 150°) on solvent polarity [(**2**)/(**3**) = 21/79 (decane), 16/84 (diglyme), 13/87 (dimethylformamide)] also suggests considerable dipolar character in the transition state for ring cleavage.

** No more than 0·5% of *cis*-(**3**) ($n = 1$ or 2) could have been formed.

[1] For one particularly thorough study, see P. S. Skell, *J. Amer. Chem. Soc.*, 1969, **91**, 7131.

[2] Cyclopropylcarbene reactions are reviewed in W. Kirmse, 'Carbene Chemistry,' 2nd edn., Academic Press, New York, 1971, pp. 467—473.

[3] P. K. Freeman and D. G. Kuper, *J. Org. Chem.*, 1965, **30**, 1047.

[4] See S. W. Staley and W. G. Kingsley, *J. Amer. Chem. Soc.*, 1973, **95**, 5804, and references therein.

[5] R. Hoffmann, G. D. Zeiss, and G. W. Van Dine, *J. Amer. Chem. Soc.*, 1968, **90**, 1485.

[6] A 'non-linear cheletropic' process: R. B. Woodward and R. Hoffmann, 'The Conservation of Orbital Symmetry,' Academic Press, New York, 1970, pp. 152—163.