

Eliminative Ring Fission of Cyclobutanes: Evaluation of Acceleration by Strain and the Comparison with Cyclopropanes

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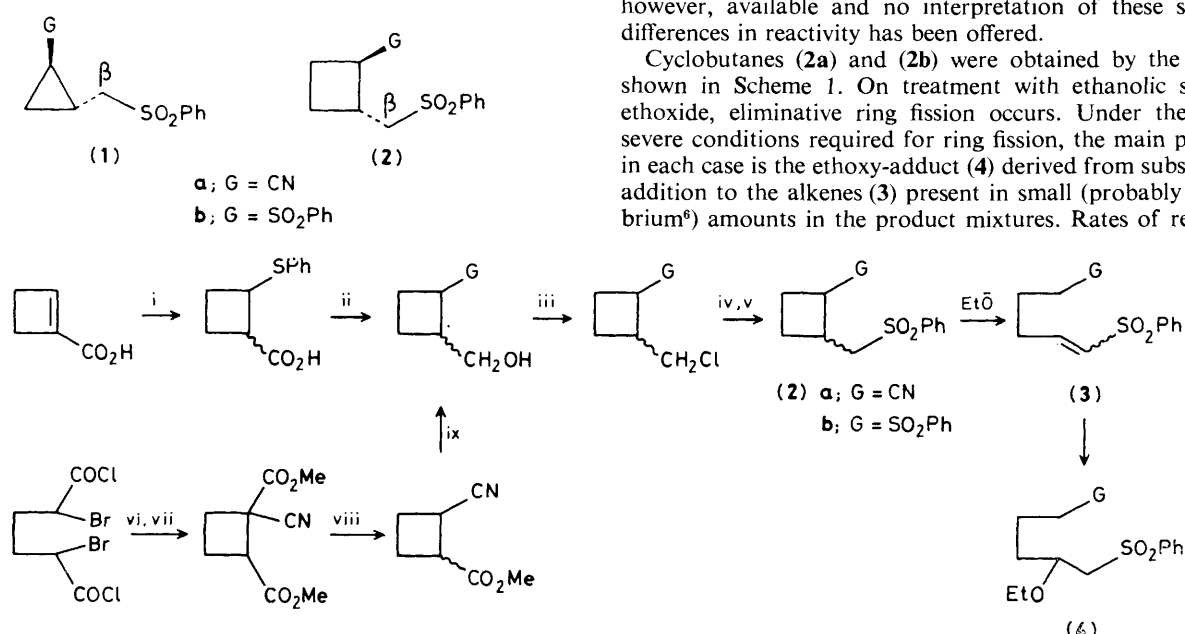
Cyclobutanes, by comparison with cyclopropanes, are reluctant to undergo eliminative ring fission; the very similar strain energies are released differently in the transition states for fission.

We recently reported¹ the first direct evaluation of the contribution of ring strain to the acceleration of leaving group departure in elimination reactions. The reactions studied were eliminative ring fissions in cyclopropanes (1) for which it was estimated that about 60% of the ring strain energy contributes to the lowering of the activation energy for ring fission. It was also concluded² that the degree of cleavage of the strained ring in the transition state was small because of the insensitivity of rate constant to attachment of the phenyl group on the leaving

group, despite the stabilisations known to be accorded to the discrete carbanions by the same structural alteration.

We now report a quantitative comparison of the related cyclobutanes (2) with the cyclopropanes studied earlier.^{1,2} It has been known for some time that eliminative ring fission³ of cyclobutanes appeared to be much slower than that of cyclopropanes. In particular, the susceptibility of cyclopropanols⁴ towards carbonyl-forming eliminative ring fission is markedly greater than for cyclobutanols.⁵ No quantitative data are, however, available and no interpretation of these striking differences in reactivity has been offered.

Cyclobutanes (2a) and (2b) were obtained by the routes shown in Scheme 1. On treatment with ethanolic sodium ethoxide, eliminative ring fission occurs. Under the fairly severe conditions required for ring fission, the main product in each case is the ethoxy-adduct (4) derived from subsequent addition to the alkenes (3) present in small (probably equilibrium⁶) amounts in the product mixtures. Rates of reaction

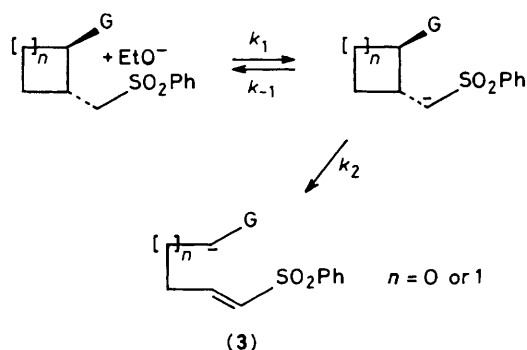


Scheme 1. i, PhSH; ii, BH₃-tetrahydrofuran; iii, SOCl₂; iv, PhS⁻Na⁺-EtOH; v, H₂O₂-MeOH-NH₄MoO₇; vi, MeOH; vii, KCN-MeOH; viii, NaCl-H₂O-Me₂SO; ix, LiBH₄.

Table 1. Eliminative ring fission in cycloalkanes.

	$k_{\text{rel}}^{\text{a}}$	$k_{\text{detrit}}^{\text{b}}$	$\Delta H^{\ddagger \text{c}}$	$\Delta S^{\ddagger \text{d}}$	Rank ^e ($\log k_{\text{obs}} - \log k_{\text{deprot}} + 11$)
(1a)	0.4	1.1×10^{-1}	104	50	8.3
(1b)	1 ^f	1.2×10^{-1}	74	-42	8.7
(2a)	8.3×10^{-5}	6.4×10^{-2}	131	71	4.9
(2b)	5.3×10^{-3}	—	98	4	6.7

^a Reactions in $\text{EtO}^- \text{Na}^+ - \text{EtOH}$ at 25 °C. Results for cyclobutanes from 4-point activation plots using rate constants obtained at higher temperatures. ^b Units: $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ for reactions in $\text{EtO}^- \text{Na}^+ - \text{EtOH}$ at 25 °C. ^c Units: kJ mol^{-1} . ^d Units: $\text{J K}^{-1} \text{mol}^{-1}$. ^e Cf. ref. 1. ^f k (25 °C) $4.7 \times 10^{-3} \text{ dm}^3 \text{mol}^{-1} \text{s}^{-1}$.



have been measured by following the disappearance of the cyclobutanes from aliquots of reaction mixtures using ^{13}C and ^1H n.m.r. spectroscopy. Results are in Table 1 together with those for cyclopropanes obtained previously.

The following features of these comparisons are notable: (i) that rates of detritiation are substantially greater than rates of ring fission, establishing that deprotonation (k_1) is not rate-determining; (ii) rate constants for ring fission of both cyclopropanes are very much greater than those of the corresponding cyclobutanes. The excess enthalpy⁷ of cyclopropane is slightly greater than that of cyclobutane and if 60%¹ of this strain energy difference were expressed as a differential between the observed rate constants, then the ratio of $k_{3-\text{ring}}^{\text{obs}} : k_{4-\text{ring}}^{\text{obs}}$ would be ca. 4. Rate constants for eliminative ring fission are the composite of the pre-equilibrium (k_1/k_{-1}) for deprotonation and the rate constant (k_2) for fission of the carbanion. Detritiation rate constants show that a negligibly small part of the difference between 3- and 4-membered rings is to be attributed to the pre-equilibrium (reprotonation of the carbanion being assumed to be diffusion controlled⁸). Detritiation rate constants for the cyclobutanes agree closely with those obtained earlier⁹ for acyclic analogues. The nucleofugality (\equiv rank) differences between 3- and 4-membered ring systems are in Table 1.

Our interpretation of these large differentials is based on a simple interpretation of the origin of strain in cyclopropanes and cyclobutanes. For the former, the excess enthalpy (115 kJ mol^{-1}) is to be attributed to valence angle distortion (ca. 75%) and repulsions between hydrogen atoms on adjacent carbon atoms (torsional strain; ca. 25%).¹⁰ In cyclobutanes, however, the almost equally large excess enthalpy (110 kJ mol^{-1}) is a composite of valence angle distortion and torsional strain, upon which is superimposed the repulsive interaction between C-1 and C-3 and between C-2 and C-4. Estimates of the importance of this interaction differ but it seems fairly clear that at least half of the excess enthalpy of cyclobutane is to be attributed to this source.^{10,11} The change in excess enthalpy as a function of extension of one bond of cyclopropane or cyclo-

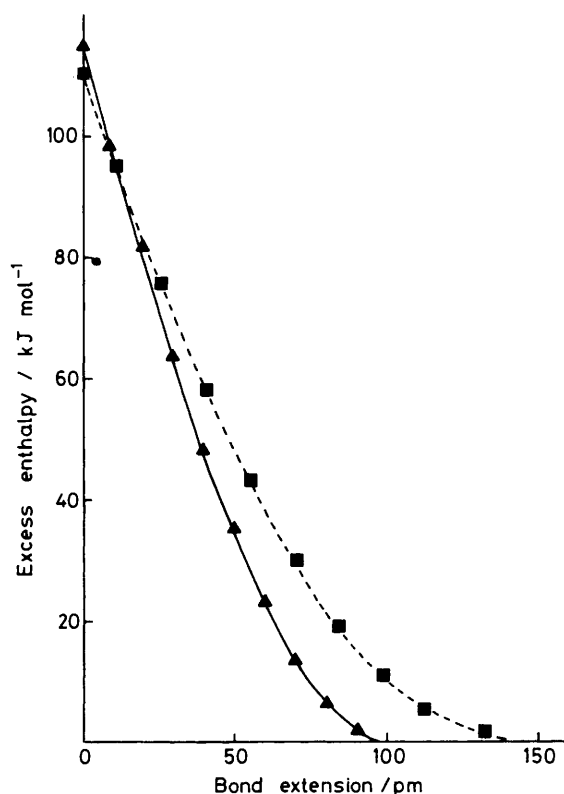


Figure 1. Excess enthalpy as a function of bond extension for: ■, cyclobutane; ▲, cyclopropane.

butane can be simply calculated (Figure 1) using considerations developed earlier.¹⁰

Figure 1 shows that the composite excess enthalpy decreases less in cyclobutane than in cyclopropane for a small bond extension. Comparison of the reactivity of cyclopropanes (1) with open-chain analogues suggests that about 60% of the excess enthalpy is released at the transition state for ring fission. Such a reduction in excess enthalpy corresponds (Figure 1) to an extension of about 45 pm to the ring bond which breaks. Similarly, for the cyclobutane (2b) the rank difference between the strained leaving group and the acyclic analogue¹ suggests a release of about 50% of the excess enthalpy at the transition state. Figure 1 shows that this also corresponds to an extension of ca. 45 pm in the bond which breaks. It can be seen that this same degree of bond extension produces substantially less reduction of strain in the four-membered than in the three-membered ring system. The activation parameters for ring fission support this general conclusion. The differential in reactivity between the two systems is the result of change

in the *enthalpy* term (Table 1). The entropy terms are more positive for cyclobutanes than for cyclopropanes; a larger number of atoms is freed from restriction as the ring opens in a cyclobutane. An abnormal ground state structure for the cyclobutanes is excluded by the *X*-ray crystal structure of (2b) which shows no significant departure from the usual dimensions of the slightly puckered ring of cyclobutane itself.

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