

Evidence for a Bridged Transition State in the Formation of β -Bromoalkyl Radicals

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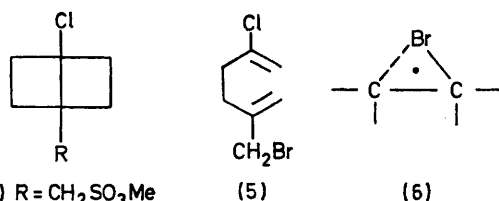
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Summary Comparison of the Arrhenius parameters for the ring-opening of 1-bromomethyl-4-chlorobicyclo[2,2,0]hexane with those for the 1-methyl and 1-ethyl derivatives indicates a reduction in E_A of 2.5 and 2.9 kcal/mol respectively, evidence for a bridged transition state in the formation of β -bromoalkyl radicals.

NEIGHBOURING-group participation by bromine has been invoked extensively in radical chemistry to explain product stereochemistry and isomer distribution in free-radical brominations,¹ reductive eliminations of vicinal dihalides using Cr^{II} complexes,² and free-radical reductions and dehalogenations of vicinal dihalides using tri-*n*-butyltin hydride.³ The postulate of a bromine substituent accelerating the abstraction of a β -hydrogen atom by way of a bridged bromine radical intermediate has been strongly refuted by Tanner *et al.*,⁴ and recent communications^{5a-g} have intensified the controversy. We present evidence here that supports the bridged radical postulate of Skell and other workers.

We have previously⁶ made a detailed kinetic study of the thermal ring opening of substituted bicyclo[2,2,0]hexanes to hexa-1,5-dienes and obtained strong evidence for the intermediacy of a cyclohexane 1,4-diradical.⁷ Although a concerted rearrangement cannot be discounted at this stage (*cf.* recent work by both Goldstein⁸ and van Rantwijk⁹), in the present context, the actual mechanism is unimportant provided that a high degree of sp^2 character is developed on the bridgehead carbon atoms in the transition complex.

The decrease in the activation energy of 2.9 kcal/mol on substituting the sterically similar bromomethyl group for an ethyl group may then be ascribed to conjugation of the non-bonding bromine electrons with those of the bridgehead carbon. This is most readily pictured as a bridged bromine radical (6) as previously used by Skell and others.¹ The stabilization energy is in excellent agreement with that of 3.0 kcal/mol obtained^{5a} recently from considering the relative reactivity to radical attack of the β -position of 1-bromobutane compared to that of propane.



(1) R = $\text{CH}_2\text{SO}_3\text{Me}$

(2) R = Me

(3) R = Et

(4) R = CH_2Br

It may be argued that a bridged intermediate of this type would decrease ΔS^\ddagger and consequently the Arrhenius A factor. However, the stabilization energy of a bridged bromine radical of 2.9 kcal/mol may alternatively be considered as the increase in the barrier height for internal rotation of the bromomethyl group about the C-C bond.

TABLE. Arrhenius parameters for ring-opening of substituted bicyclo[2,2,0]hexanes

Solvent	(2) ⁶		(3) ⁶		(4)	
	E_A	$\log A$	E_A	$\log A$	E_A	$\log A$
Tetrachloroethylene	35.50 ± 0.13^a	13.55 ± 0.31	36.19 ± 0.13	13.68 ± 0.29	33.09 ± 0.04	13.86 ± 0.10
<i>o</i> -Dichlorobenzene	35.68 ± 0.13	13.64 ± 0.30	35.87 ± 0.06	13.55 ± 0.15	33.16 ± 0.07	13.97 ± 0.17

^a Errors are least-squares deviations.

The bicyclohexane (4) was prepared by displacement of the mesylate (1), m.p. 47°, of 1-chloro-4-hydroxymethyl-bicyclo[2,2,0]hexane¹⁰ with Bu_4NBr in acetone. A detailed kinetic study of the ring-opening of (4) in both tetrachloroethylene and *o*-dichlorobenzene was carried out over the temperature range 98.6–153.5°C. Excellent first-order kinetics for the unimolecular isomerisation were obtained (by ¹H n.m.r. spectroscopy as previously described,^{6†}) the diene (5) being the only thermolysis product. Least-squares analysis gave the Arrhenius parameters in the Table.

Comparison of these Arrhenius parameters with those determined in the same solvent systems for compounds (2) and (3)⁶ shows that whereas the Arrhenius A factor is unchanged (within experimental error), substitution of the bromomethyl group for a methyl or ethyl group reduces the activation energy by 2.5 and 2.9 kcal/mol respectively.

The decrease in entropy of a free rotor as a function of barrier height has been tabulated by Lewis and Randall.¹¹ The effect of an increase of 2.9 kcal/mol for the bromomethyl group is dependent upon the initial barrier height in the bicyclo[2,2,0]hexane molecule. The minimum value is 3.6 kcal/mol as in bromoethane.¹² An increase of barrier height to 6.5 kcal/mol would decrease the experimental ΔS^\ddagger by 0.8 cal $\text{K}^{-1} \text{mol}^{-1}$ and $\log A$ by 0.17. However, previous results suggest that there is steric interaction of 1,4-substituents in the bicyclo[2,2,0]hexane molecule,⁶ any increase in the initial barrier height will decrease the effect on ΔS^\ddagger of a barrier height increase of 2.9 kcal/mol. Consequently, the decrease in ΔS^\ddagger due to formation of a bridged structure will be small and well within the error of present experimental Arrhenius parameter determinations. It may be concluded that the similarity of the ΔS^\ddagger values determined for the isomerization of the 4-methyl-, 4-ethyl-,

† The bromomethyl signal(s) provided an inbuilt internal standard for checking calculations.

and 4-bromomethyl-1-chlorobicyclo[2,2,0]hexanes is in agreement with the β -bromomethyl stabilization energy of 2.9 kcal/mol obtained from the activation energies.

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