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ON THE RING-OPENING OF BICYCLO[2.2.0]HEXANES TO 1,5-HEXADIENES

E.N. Cain

Research School of Chemistry, Australian National University,
P.O. Box 4, Canberra, A.C.T. 2600, Australia

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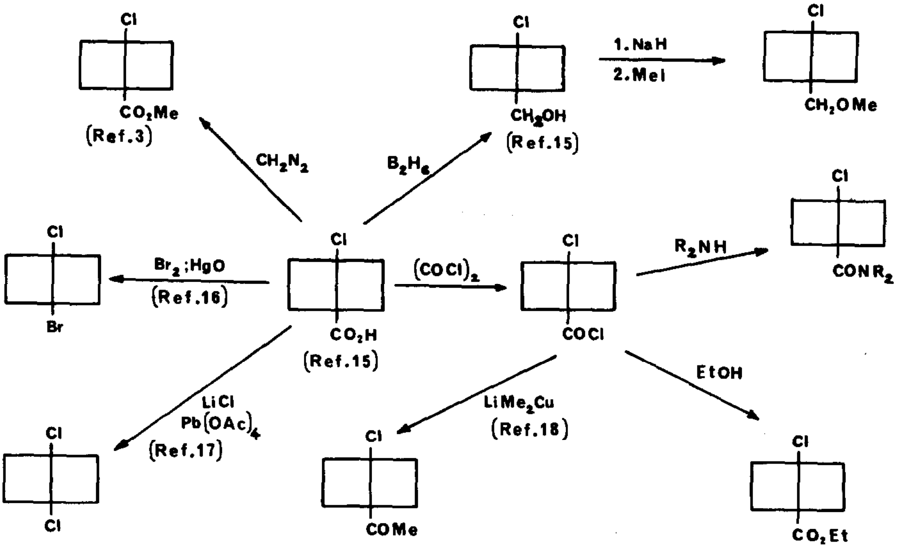
Bicyclo[2.2.0]hexanes are known to thermally open to 1,5-hexadienes[1-5] but the mechanistic pathway is still uncertain. A concerted symmetry-allowed ($\sigma^2_s + \sigma^2_a$) ring-opening process[6] requires considerable distortion and non-bonded interaction at the transition state (i) in order to achieve conservation of orbital symmetry and hence, a priori, the reaction pathway having the lowest activation energy would most probably involve a diradical species. Results by Cohen *et al*[1] on the observed activation energy (36 kcal.mole^{-1}) for the ring-opening of bicyclo[2.2.0]hexane itself shed little light on the mechanism since no thermodynamic heats of formation have yet been determined in this system (a rough value for the C-C bridgehead dissociation energy based on simple ring-strain additivity was estimated to be 31 kcal.mole^{-1}). Recent detailed theoretical calculations by Benson[7] have estimated the activation energy for bicyclo[2.2.0]hexane to be 36 kcal.mole^{-1} on the basis of a diradical intermediate with the transition state along the reaction coordinate for ring-opening to the diradical.

(i)

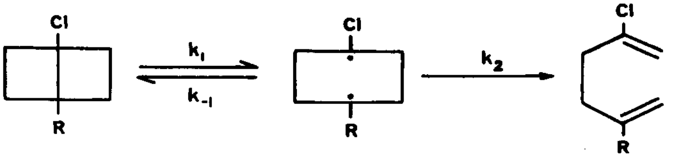
In certain ring-fused cyclobutanes both Frey[8] and Baldwin[9] have shown that the symmetry-allowed ($\sigma^2_s + \sigma^2_a$) concerted ring-opening was not observed to any marked extent, and both workers suggested a diradical as the major reaction intermediate. In a recent communication, Paquette[4] examined the stereochemical course of ring-opening of three isomeric bicyclo[2.2.0]-hexanes and despite the unique stereochemical results, suggested the possibility that "the high level of antarafaciality attained by one of the double bonds during the pyrolysis of bicyclo[2.2.0]hexane derivatives, although predicted from orbital-symmetry considerations, is actually the result of a two-step process". These results, together with Benson's recent theoretical calculations[7], prompt us to report kinetic evidence supporting this mechanism.

We have synthesised (see below) a number of different bicyclo[2.2.0]hexanes[10] each having two bridgehead substituents. All the compounds had a common substituent at the 1-position (chloro) and the functional groups at the 4-position were chosen to cover a range of substituent effects. The bicyclo[2.2.0]hexanes were heated[11] in tetrachloroethylene at 122°. Diene formation was monitored by ^{1}H n.m.r. spectroscopy and in all cases, clean apparently first-order kinetics[12] were observed and 1,5-hexadienes[10] were the only observed products. The ethyl ester (1; R = COOEt) was also heated at 98° in decalin, tetrachloroethylene, dimethylsulphoxide and N-methyl formamide (dielectric constants[13] 2.2, 2.3, 48.9 and 182.4 respectively) and the apparent first-order rate constant was the same in all four solvents and showed no increase with increasing solvent polarity. Activation parameters ($\Delta H^{\ddagger}$ = 29 kcal. mole^{-1}; $\Delta S^{\ddagger}$ = 0 e.u.) were obtained for the ethyl ester (1; R = COOEt) by kinetic studies at varied temperatures in dimethylsulphoxide ($k_{obs.}$ at 80° = 1.1×10^{-5} sec.$^{-1}$; $k_{obs.}$ at 98° = 8.7×10^{-5} sec.$^{-1}$; $k_{obs.}$ at 122° = 8.8×10^{-4} sec.$^{-1}$).



An examination of the Table below and molecular models indicated no correlation between steric interactions in the different bicyclo[2.2.0]hexanes and the rate of ring-opening. The effect of substituents on the rate of ring opening ruled strongly against an isopolar concerted reaction pathway (which would be relatively insensitive to substituents) and suggested that the intermediate involved was either a diradical or a charged species. The insensitivity of the rate of ring-opening to solvent polarity and the zero entropy of activation in a highly polar solvent (dimethylsulphoxide) both clearly indicated that negligible charge separation was developing at the transition state and thus supported a diradical intermediate. The overall results clearly showed two classes of substituent - those having a carbonyl moiety attached to the 4-position and those without. The compounds that had a carbonyl moiety showed greatly enhanced rates. This was in agreement with results recently obtained by Timberlake[14] which showed in kinetic studies on the decomposition of a series of azomethanes (a known radical reaction) that an α-carboethoxy group was responsible for a rate enhancement of 2.58×10^5 (relative to methyl). Similar radical stabilisation by a carbonyl group has been reported by other workers[19,20]. Using Benson's treatment[7] for the ring-opening of small ring compounds, the reaction scheme shown would apply and steady-state treatment then gives $k_{obs.} = \frac{k_1k_2}{k_{-1}+k_2}$.

1; R =	$k_{obs.}$ (122°)	Rel. rate (122°)	$\Delta G^{\ddagger}$ (122°)
COCl	7.0×10^{-3} sec.$^{-1}$	8050	27.3 kcal.mole^{-1}
COMe	1.8×10^{-3}	2070	28.3
COOEt	8.8×10^{-4}	1010	28.9
COOMe	7.9×10^{-4}	910	29.0
COOH	7.7×10^{-4}	885	29.0
CONMe$_2$	2.8×10^{-4}	320	29.8
Cl	6.3×10^{-6}	7.2	32.8
Br	3.2×10^{-6}	3.7	33.3
CH$_2$OMe	8.7×10^{-7}	1	34.3



(1) (2)

As Benson has stated for the parent bicyclo[2.2.0]hexane system, the most probable situation would be $k_2 \gg k_{-1}$ ($k_{obs.} \approx k_1$). The other possibilities would be $k_{-1} \approx k_2$ (by analogy with the monocyclic cyclobutanes[21] in which case $k_{obs.} \approx \frac{1}{2}k_1$) and, less likely, $k_{-1} \gg k_2$ ($k_{obs.} = \frac{k_1k_2}{k_{-1}}$). In all cases, the actual observed rates would be related to the stability of the diradical.

We feel that the above kinetic results combine to strongly substantiate the intermediacy of a diradical in the ring-opening of bicyclo[2.2.0]hexanes.

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10. All new compounds gave satisfactory elemental analyses and all spectra were in accord with assigned structures.
11. Samples were dissolved (ca. 15%) in tetrachloroethylene and sealed in n.m.r. tubes after thorough degassing using the freeze-thaw technique.
12. Considering the inherent limitations of n.m.r. for following reaction kinetics, the rate constants would contain an error of ca. ± 5%.
13. Dielectric constants for tetrachloroethylene and decalin from "Techniques of Organic Chemistry. Vol. VII. Organic Solvents", Ed. A. Weissberger, Interscience, New York, 1965, and for dimethylsulphoxide and N-methylformamide from A.J. Parker in "Advances in Physical Organic Chemistry", Vol. 5, Ed. V. Gold, London, 1967, p.173.
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