Syntheses and Equilibria of Fused Bicyclic Methylenecyclopropanes

By Andrew S. Kende* and Edgar E. Riecke

(Department of Chemistry, University of Rochester, Rochester, New York 14627)

Summary Isomeric bicyclic methylenecyclopropanes, obtained from carbenoid ring contraction of bicyclic cyclobutanones, exhibit extraordinarily clean thermal equilibria which is entropy-controlled near the boundaries of Bredt's rule.

Recent work has highlighted the limits of stability for methylenecyclopropanes fused within a bicyclic system. It is clear from the studies of Berson's group that the bicyclopentane (1), not isolable under normal conditions, undergoes spontaneous dimerization via a trimethylenemethane intermediate which can be detected by CIDNP.[1] Kobrich has likewise noted that its bicyclohexene counterpart (2) is only briefly stable in solution.[2] We report the preparations of five new unsubstituted hydrocarbons of this series, including the remarkably stable bicyclohexane (3), and to comment on a hitherto unspecified factor controlling their intramolecular isomerisation equilibria.

Our general synthesis of fused methylenecyclopropanes employs carbenoid ring contraction of bicyclic cyclobutanone toluenesulphonylhydrazones, themselves available via 2+2 addition of dichloroketen to olefins. Thus, addition of dichloroketen[3] to cyclohexene gave 39% of adduct (4) (b.p. 60° at 0·1 mmHg) accompanied by a 5% yield of an unidentified $C_{10}H_{10}Cl_4O_2$ byproduct (b.p. 110° at 0·1 mm Hg). Dehalogenation (Zn–AcOH) of (4) at room temperature for 24 h gave exclusively the cyclobutanone

(5) (b.p. 81° at 25 mm Hg), characterized as the toluenesulphonylhydrazone (6), m.p. 103—105°.†

(1)   (2)   (3)

(4) R=Cl, X=O
(5) R=H, X=O
(6) R=H, X=NNHSO₂C₇H₇

(7a)   (7b)

(8a)   (8b)   (9)
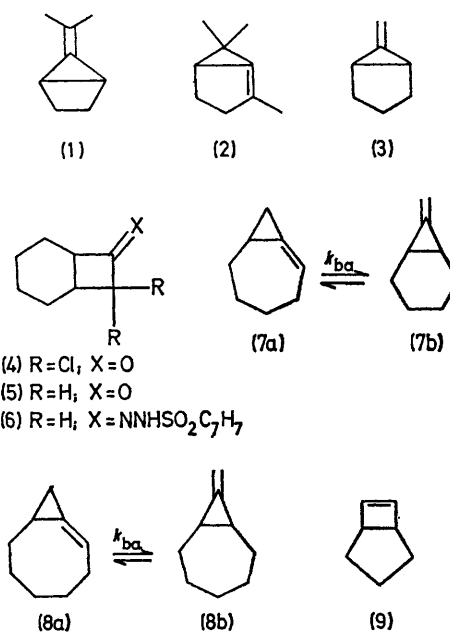
† All new compounds gave satisfactory analytical data or mass spectra.

Pyrolysis of the dry lithium salt of (6) at 120—180° and 0·1 mm Hg produced *ca.* 50% of a 2·0:1·0 mixture of methylenecyclopropanes identified as (7a) and (7b), respectively, by mass and n.m.r. spectroscopy, and by di-imide reduction to the corresponding known C_8H_{14} bicyclic hydrocarbons.[4]

A parallel reaction sequence starting from cycloheptene produced a 1·0:1·1 mixture of the methylenecyclopropanes (8a) and (8b), readily differentiated by n.m.r. spectroscopy.‡

the Table, differed markedly from the kinetic ratios obtained from the tosylhydrazone pyrolyses, suggesting that migration of the more substituted σ-bond is preferred in the early transition states of these exothermic carbenoid rearrangements.[6]

The parallel between the strain in a system such as (7a) and that of an anti-Bredt[7] bridgehead bicyclo[4,1,1]octene has been suggested.[8] It is, therefore, noteworthy that the preference of (7b) over (7a) at equilibrium does not arise

TABLE[a]

Starting isomer	T/°C	$k \times 10^5$ $(\pm\sigma)$/s^{-1}	$\Delta H\ddagger$ (kcal/mol)	$\Delta S\ddagger$ (cal/deg/mol)	K(b/a)	$\Delta H°$ (kcal/mol)	$\Delta S°$ (cal/deg/mol)
(7a)	180·0	10·4 ± 0·1	35·2 ± 0·5	0·15 ± 1	13·37	2·97	11·69
	197·1	44·8 ± 0·5			15·07		
(7b)	180·0	0·779 ± 0·007	32·2 ± 0·5	11·65 ± 1			
	197·1	2·94 ± 0·03					
(8a)	231·2	4·07 ± 0·04	41·7 ± 0·6	2·94 ± 1	0·6426	2·58	4·22
	245·9	13·6 ± 0·1			0·6641		
(8b)	231·2	6·33 ± 0·06	40·6 ± 0·7	1·61 ± 1			
	245·9	20·5 ± 0·2					

[a] Kinetic pyrolyses were carried out in sealed Pyrex tubes using hexane as solvent and decane as a g.l.c. internal standard, and were followed by g.l.c. First-order kinetics were obeyed in all equilibria. Each rate constant was determined from five samplings taken at intervals up to a *ca.* 50% conversion toward equilibrium concentrations. Equilibrium constants were determined from samplings taken at *ca.* 99·8% conversions toward equilibrium concentrations. The ranges for $\Delta H\ddagger$ and $\Delta S\ddagger$ are maximum errors calculated from the deviations in rate constants, as determined by a linear regression analysis program.

In a sequence starting with cyclopentene, on the other hand, only the methylenecyclopropane (3) could be detected [δ 5·18 (2H, s) and 1·67 (8H, m)] along with bicycloheptene (9) [δ 5·72 (2H, s), 3·10 (2H, d, J 6 Hz), and 1·48 (6H, m)][5] in a 2·8:1·0 ratio.

In the case of (7) and (8) a very clean thermal equilibrium between the isomers could be established, whereas (3) gave neither equilibrium isomers nor dimers up to 231° [$t_{\frac{1}{2}}$ (231°) 7·7 h]. Equilibrium ratios (7b/7a) and (8b/8a), shown in

from enthalpy effects associated with Baeyer strain[9] or torsional effects. It arises exclusively from the more negative entropy of the highly rigid isomer (7a) ($\Delta S°$ = 11·69 cal/deg/mol). Presumably this phenomenon plays a controlling role in the reactions of more conventional systems at the boundaries of Bredt's rule.

(Received, 17th October 1973; Com. 1429.)

‡ (8a) δ 5·73 (1H, m) and 2·2—0·5 (13H, m); (8b) δ 5·50 (0·82H, s), 5·18 (1·18H, s), and 2·8—1·0 (12H, m). *cis-* and *trans-*Cyclopropane ring junctions are distinguished by n.m.r. spectroscopy (*viz.* δ 5·50 and 5·18) but the isomers were not separated during purification.

[1] J. A. Berson, R. J. Bushby, J. M. McBride, and M. Trembling, *J. Amer. Chem. Soc.*, 1971, 93, 1544.
[2] G. Kobrich and H. Heinemann, *Chem. Comm.*, 1969, 493.
[3] L. Ghosez, R. Montaigne, A. Roussel, H. Vanlierde, and P. Mollet, *Tetrahedron*, 1971, 24, 615.
[4] *endo-*7-Methylnorcarane: W. L. Pilling and F. Y. Edamura, *J. Org. Chem.*, 1967, 32, 3492; bicyclo[5,1,0]octane: J. G. Traynham, J. S. Dehn, and E. Green, *J. Org. Chem.*, 1968, 33, 2587.
[5] O. L. Chapman, D. J. Pasto, G. W. Borden, and A. A. Griswold, *J. Amer. Chem. Soc.*, 1962, 84, 1220.
[6] W. Kirmse, 'Carbene Chemistry,' 2nd Edn., Academic Press, 1971, pp. 457—463; 467—475.
[7] J. Bredt, *Annalen*, 1924, 437, 1.
[8] G. Kobrich and M. Baumann, *Angew. Chem. Internat. Edn.*, 1972, 11(1), 52.
[9] A. von Baeyer, *Ber.*, 1885, 18, 2277.