trans-Cycloalkenes. Part 7.[1] Variable Temperature ^{13}C Nuclear Magnetic Resonance Studies on *cis,trans*-Cyclo-octa-1,5-diene and Related Compounds

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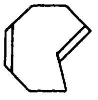
cis,trans-Cyclo-octa-1,5-diene (1) and the derived *trans*-bicyclo[6.1.0]non-4-ene (3) and its 9-oxa- (2) and 9-phenyl-9-aza- (3) analogues show temperature-dependent ^{13}C n.m.r. spectra which are interpreted in terms of a conformational ring inversion process. The energy barriers for this process for compounds (1)—(4) are estimated to be 35, 41.5, 45, and 44.5 kJ mol^{-1}, respectively.

IN the course of some synthetic work on *trans*-cyclo-octenes, *cis,trans*-cyclo-octa-1,5-diene (1) became readily available.[2] A preliminary examination of its ^{13}C n.m.r. spectrum revealed marked temperature dependence, and it was decided to investigate this more fully. The corresponding epoxide (2), cyclopropane (3), and *N*-phenylaziridine (4) were studied for comparison.



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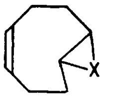


(2) X = O
(3) X = CH$_2$
(4) X = NPh

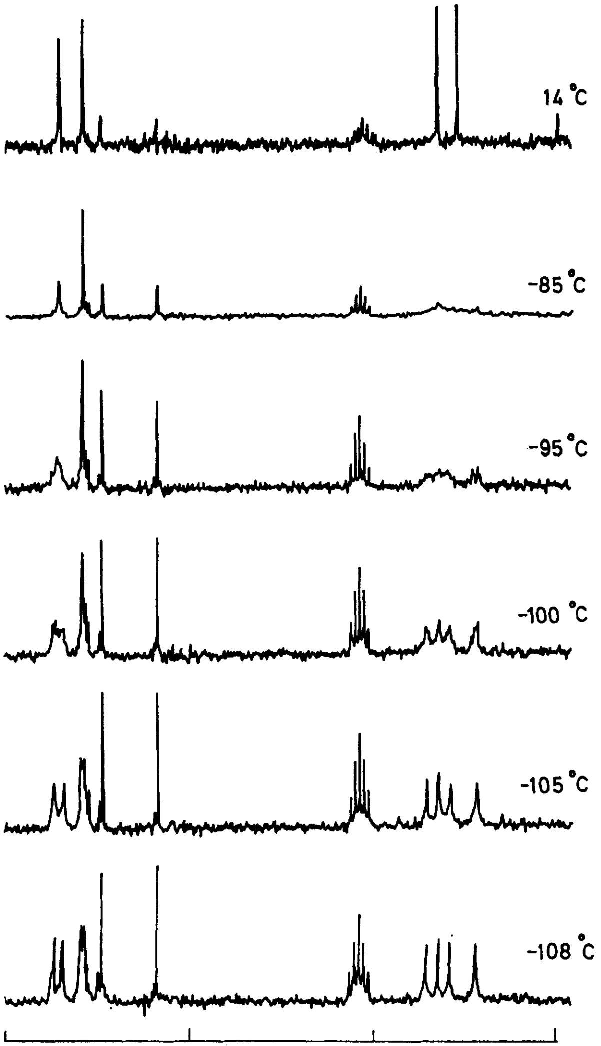
EXPERIMENTAL

cis,trans-*Cyclo-octa*-1,5-diene.—This was prepared[2] by the hydroxyphosphine oxide method.[3] G.l.c. (15% Carbowax on Diatomite C-AW) showed *ca.* 1% of the *cis,cis*-isomer.

(1RS,8RS)-9-*Oxabicyclo*[6.1.0]*non*-4-*ene* (2).—*cis,trans*-Cyclo-octa-1,5-diene (3.4 g, 0.031 mol) in methylene chloride (80 ml) over sodium carbonate (5 g) was epoxidised with peracetic acid [45%; 6 ml, containing sodium acetate trihydrate (1.2 g)] at 25 °C. Stirring was continued for 90 min before water (100 ml) was added. The product was isolated with methylene chloride and distilled to give the *epoxide* (2.5 g, 66%), b.p. 68—72 °C at 12 mmHg (Found: C, 77.0; H, 9.6. $C_8H_{12}O$ requires C, 77.4; H, 9.7%), τ 4.1—4.5 (2 H, m, 4- and 5-H), 7.2—7.6 (2 H, m, 1- and 8-H), and 7.6—9.2 (8 H, m).

(1RS,8RS)-*Bicyclo*[6.1.0]*non*-4-*ene* (3).—*cis,trans*-Cyclo-octa-1,5-diene (600 mg, 5.5 mmol) in ether (10 ml) was treated dropwise with freshly distilled diazomethane in ether. The diazomethane was rapidly consumed and the reaction was judged complete when the yellow colour persisted and g.l.c. showed the absence of *cis,trans*-diene. The slight excess of diazomethane was removed in a stream of nitrogen. Evaporation followed by distillation gave (1RS,8RS)-9,10-*diazabicyclo*[6.3.0]*undeca*-4,9-*diene* (650 mg, 78%), b.p. 90 °C (bath) at 3 mmHg (Found: C, 71.7; H, 9.4; N, 18.4. $C_9H_{14}N_2$ requires C, 72.0; H, 9.3; N, 18.7%).

This diazomethane adduct (500 mg) in light petroleum (b.p. 30—40 °C; 125 ml) was irradiated under reflux with a mercury vapour lamp (500 W) for 5 h. The cooled solution was filtered and evaporated. Distillation gave the *bicyclic olefin* (3) (261 mg, 64%) as an oil, b.p. 60 °C (bath) at 10 mmHg (Found: C, 88.2; H, 11.5. C_9H_{14} requires C, 88.5; H, 11.6%), τ (CCl_4) 4.3 (2 H, m, =CH), 7.5—8.1 (6 H, m), and 9.0—9.7 (6 H, m).



^{13}C N.m.r. spectra of *cis,trans*-cyclo-octa-1,5-diene

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[1] Part 6, R. C. Hayward and G. H. Whitham, *J.C.S. Perkin I*, 1975, 2267.

[2] P. F. Newton, unpublished work.

[3] A. J. Bridges and G. H. Whitham, *J.C.S. Chem. Comm.*, 1974, 142.

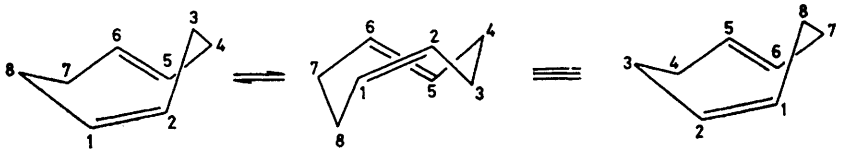
(1RS,8RS)-9-*Phenyl*-9-*azabicyclo*[6.1.0]*non*-4-*ene* (4).—*cis,trans*-Cyclo-octa-1,5-diene (500 mg) and phenyl azide (580 mg) in light petroleum (b.p. 40—60 °C; 20 ml) was set aside at 20 °C for 1 h. The resulting crystalline triazoline was collected (960 mg, 90%), m.p. 102 °C (decomp.) (lit.,[4] 102—103°) (Found: C, 73.7; H, 7.6; N, 18.9. Calc. for $C_{14}H_{17}N_3$: C, 74.0; H, 7.5; N, 18.5%). The triazoline (500 mg) in light petroleum (50 ml) was irradiated with a mercury vapour lamp for 4 h. The solution was filtered and evaporated, and the residue distilled to give the *aziridine* (4) (300 mg, 68%), b.p. 100 °C (bath) at 2 mmHg (Found: C, 84.1; H, 8.9; N, 6.9. $C_{14}H_{17}N$ requires C, 84.4; H, 8.6; N, 7.0%), τ 2.75—3.3 (5 H, m, Ph), 4.32 (2 H, m, CH=), 7.4—8.1 (8 H, m), and 8.7—9.2 (2 H, m).

^{13}C *N.m.r. Spectra*.—Pulse Fourier transform ^{13}C n.m.r. spectra were recorded with a Bruker WH90 instrument operating at 22.63 MHz, using broad band proton decoupling. Variable temperature runs were carried out for 10% solutions in CD_2Cl_2–CCl_3F (1 : 1). Solvent peaks are marked in the Figure by an arrow (↑) on the scale. Chemical shifts are quoted in p.p.m. downfield of internal tetramethylsilane.

RESULTS AND DISCUSSION

The effect of temperature on the ^{13}C n.m.r. spectrum of *cis,trans*-cyclo-octa-1,5-diene is illustrated in the Figure. At room temperature only four lines were observed. On cooling, each of these lines broadened considerably and then split into a pair of lines equally spaced about the original line. At −108 °C an eight-line spectrum was obtained, and on raising the temperature the four pairs of lines coalesced to the original four singlets.

These results are interpreted in terms of a conformational ring inversion process. A molecular model of *cis,trans*-cyclo-octa-1,5-diene indicates that the preferred conformation is as in (5a). Flipping of the *cis*-double bond unit leads to (5b), which is seen to be identical to (5a) by rotation, the overall effect of the flipping process being to interchange the carbon pairs 1 and 2, 3 and 8, 4 and 7, and 5 and 6. When flipping is rapid the molecule has a time-averaged C_2 axis of symmetry, thus explaining the four-line ^{13}C n.m.r. spectrum at 14 °C. When flipping is relatively slow, however, no two carbon atoms are equivalent, leading to an eight-line spectrum.



(5a) (5b)

The Table lists coalescence temperatures and frequency separations for each of the pairs of lines. Since the simplified equation for the rate constant for conformational exchange (k_c) [$k_c = \pi(\Delta\nu)/\sqrt{2}$] can be applied to the case of equally intense coalescing singlets,[5] free energies of activation ($\Delta G^\ddagger$) can be obtained therefrom by application of the Eyring equation. The values of $\Delta G^\ddagger$ are also given in the Table, leading to a value of 35 ± 1 kJ mol^{-1} for $\Delta G^\ddagger_{180}$ for the conformational ring inversion process for *cis,trans*-cyclo-octa-1,5-diene.

Similar variable temperature spectra were obtained for the epoxide (2) and the cyclopropane (3), and they were similarly interpreted. Coalescence temperatures and derived energy barriers are given in the Table.

Coalescence temperatures and derived free energy barriers

	Line 1 [a]	Line 2	Line 3	Line 4
cis, trans-Diene (1)				
δ (278 K)	136.4	129.9	33.0	27.4
T_c/K	176	169	183	187
$\Delta\nu$ (165 K)/Hz	61.0	17.1	151.4	240.5
$\Delta G^\ddagger$/kJ mol^{-1}	35	35.5	35	35
Epoxide (2)				
δ (283 K)	130.7	58.9	29.1	25.5
T_c/K	198	202	210	204
$\Delta\nu$ (185 K)/Hz	24.4	36.6	113.5	45.2
$\Delta G^\ddagger$/kJ mol^{-1}	41.5	41.5	41	41.5
Cyclopropane (3)				
δ (283 K) [b]	131.0	30.2	28.2	18.7
T_c/K	216	227	216	209
$\Delta\nu$ (183 K)/Hz	22.0	81.8	28.1	13.4
$\Delta G^\ddagger$/kJ mol^{-1}	45	45	44.5	44.5
Aziridine (4)				
δ (283 K)	130.7	45.4	27.6	26.0
T_c/K	210	242		208
$\Delta\nu$ (183 K)/Hz	15.9	91.6		14.65
$\Delta G^\ddagger$/kJ mol^{-1}	44.5	48		44.5

[a] The four lines in the room temperature spectrum due to ring carbon atoms are numbered from low to high field. [b] δ 13.8 p.p.m. (C-9).

The aziridine (4) proved more complex: two sets of coalescence phenomena were observed in the ^{13}C n.m.r. spectra in the temperature range examined. This indicates that in addition to the ring flipping process found in the previous compounds, a second conformational process is occurring, presumably inversion about nitrogen in the aziridine ring. Either process leads to interconversion of two non-equivalent conformations, (6) and (7). Inversion at nitrogen interchanges carbon atoms 1,2,3 . . . of (6) with 1,2,3 . . . of (7), whereas double bond flipping interchanges 1,2,3 . . . of (6) with 8,7,6 . . . of (7). When both processes occur sufficiently rapidly the molecule possesses an averaged C_2 symmetry axis, thus accounting for four signals for the eight-membered ring carbon atoms in the room temperature ^{13}C n.m.r. spectrum. On cooling the splittings which occur depend on the frequency separation of the signals (or signal averages) due to the carbon atoms being

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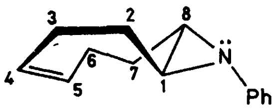
[4] K. Ziegler and H. Wilms, *Annalen*, 1950, **567**, 1.

[5] G. Binsch, *Topics Stereochem.*, 1968, **3**, 97; I. O. Sutherland, *Ann. Reports N.M.R. Spectroscopy*, 1971, **4**, 71; D. Kost, E. H. Carlson, and M. Raban, *Chem. Comm.*, 1971, 656.

interchanged, and the energy barriers of the processes causing the interchange.



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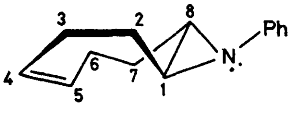

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It is found that line 1 (olefinic carbons) splits on cooling into a doublet, and line 2 (allylic carbons) into a doublet the lines of which each split again at lower temperatures. This second splitting gives lines of unequal intensity owing to the unequal populations of conformations (6) and (7). For line 3 (homoallylic carbons) both coalescences occur in the same temperature range, the broadened line giving four signals on further cooling. Line 4 (bridgehead carbons) splits only once in the temperature range examined.

The approximate expression for k_c cannot be used for lines which split into components of unequal populations, *i.e.* for line 3 or for the second coalescence of line 2, but was used for the first coalescences of lines 1, 2, and 4, and the rate constants and derived energy barriers are given in the Table. Two of the values for energy barriers are similar to those obtained for the epoxide (2) and cyclopropane (3), and were attributed to the double bond flipping process. The other value, 48 kJ mol^{-1}, is close to that expected for nitrogen inversion in an aziridine (*cf.* 50 kJ mol^{-1} for *N*-phenylaziridine [6]) and was assigned as such. If ring flipping, as monitored by the spectral changes for line 2, is occurring rapidly on the ^{13}C n.m.r. time scale, then nitrogen inversion interconverts equally populated conformers. It is thus fortuitous that the energy barriers and frequency differences are such as to allow $\Delta G^{\ddagger}$ values for both processes to be measured.

Cope *et al.*[7] had previously considered the possibility of a conformational ring flipping process for the *cis,trans*-diene (1), but were unable to find any evidence from variable temperature ^{1}H n.m.r. spectroscopy. A recent paper depicts the ^{13}C n.m.r. spectrum of 1,2,5,6-tetracyano-*cis,trans*-cyclo-octadiene.[8] This shows four ring carbon signals at +61 °C with seven at −44 °C, and although no coalescence temperatures were given it is clear from the small $\Delta\nu$ values and the relatively high temperature at which coalescence must be occurring that the energy barrier for ring inversion here must be considerably greater than for the parent diene. There seems no obvious reason why this should be so.

It is noteworthy that the free energy of activation for the ring inversion process is higher for the three-membered ring derivatives (2)—(4) than for the parent diene (1). This may be due to release of torsional strain in going from the *trans*-double bond to the three-membered ring, thereby lowering the energy of the ground state relative to the transition state for *cis*-double bond flipping.

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[7/016 *Received, 5th January,* 1977]

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[6] F. A. L. Anet and J. M. Osyany, *J. Amer. Chem. Soc.*, 1967, **89**, 352.

[7] A. C. Cope, C. F. Howell, J. Bowers, R. C. Lord, and G. M. Whitesides, *J. Amer. Chem. Soc.*, 1967, **89**, 4024.

[8] D. Bellus, H.-C. Mez, G. Rihs, and H. Sauter, *J. Amer. Chem. Soc.*, 1974, **96**, 5007.