

## Conformational Studies on the Bicyclo[3.3.2]Decane System

By Martin Doyle,<sup>a</sup> Russell Hafter,<sup>b</sup> and William Parker,<sup>a,b</sup> <sup>a</sup> School of Physical Sciences, New University of Ulster, Coleraine, County Londonderry, Northern Ireland, and <sup>b</sup> Department of Chemistry, University of Stirling, Stirling 4K9 4LA, Scotland

The spectral properties of a series of bicyclo[3.3.2]decane derivatives have been examined, and the occurrence, in certain cases, of abnormal  $\delta(\text{CH})$  and  $\nu(\text{CH})$  i.r. absorptions attributed to a C-3, C-7 transannular methylene interaction in a twin-chair conformation. There is some evidence for a twin-chair  $\rightleftharpoons$  boat-chair equilibrium, and data from reduction of the 3-one by dissolving metals reveals essentially no free energy difference between these conformers. In cases where the two-carbon bridge is constrained by a double bond, or its equivalent, such that C-1, C-9, C-10, and C-5 are coplanar, the preferred conformation is boat-chair as confirmed by an X-ray crystal analysis of 7,8,9,10-tetrahydro-6,10-propano-6H-cyclohepta[b]quinoxaline. When this ring system carries an ethano-bridge, the question of whether there is an eclipsed or staggered arrangement around C-9, C-10 is discussed in the light of u.v. and n.m.r. studies and the corresponding situation in homoadamantane, where an X-ray structure of the 1,8-bismethoxycarbonyl derivative has revealed a virtually eclipsed arrangement.

For some time in these laboratories studies have been in progress aimed at evaluating the various factors which influence transannular hydride migrations; for example, results from the bicyclo[3.3.1]nonan-3-yl<sup>1</sup> and cyclooctyl<sup>2</sup> systems have helped to clarify the roles played by ring strain and proximity of the C-H bond to the developing cationic centre. Further studies<sup>3</sup> on suitable bicyclo[3.3.2]decane substrates were then called for, and a ground-state conformational picture<sup>4</sup> of this ring system was needed before meaningful comments on its reactivity could be made.

The six most likely conformations of the parent hydrocarbon (1a) are illustrated in the Scheme.

(a) *The twin twist-chair.* This form, with a staggered two-carbon bridge, has a severe transannular interaction between the *endo* C-3 and C-7 hydrogen atoms, with additional smaller repulsions between positions 2 and 10, and 6 and 9. The major repulsions can be alleviated to a certain extent by easing both rings outwards; indeed a Dreiding model of this conformation is quite flexible.

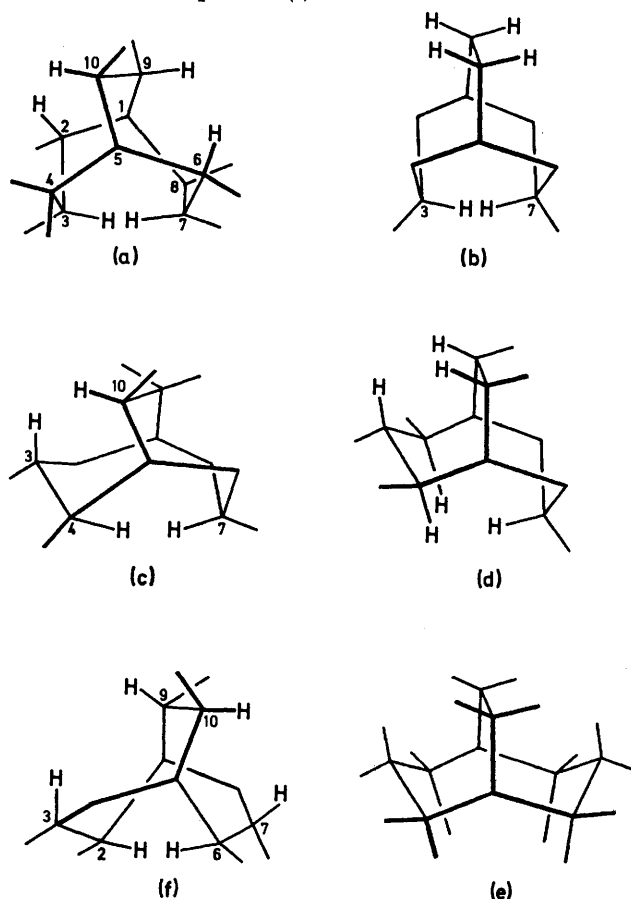
(b) *The eclipsed twin-chair.* This has an untenable 3,7-interaction. A model shows that the *endo*-hydrogen atoms are separated by only 10 pm, with an associated C-3,C-7 interatomic distance of 210 pm. There is also considerable torsional and angle strain stemming from the eclipsed two-carbon (C-9, C-10) bridge. A Dreiding model of this conformation is mechanically unstable with respect to (a).

(c) *The twist boat-chair.* This has two transannular interactions, *viz.* between the hydrogen atoms on C-3 and C-10 (80 pm separation) and those on C-4 and C-7 (110 pm). Any attempt to relieve these tensions by flexing the molecule only serves to create new, equally severe strains.

(d) *The eclipsed boat-chair.* This is characterised by the same eclipsed two-carbon bridge and associated bond angle and torsional strain as in (b). There are also smaller transannular interactions between the hydrogen atoms on C-3 and those on C-9 and -10 and between C-7 and C-2 and -4.

(e) *The eclipsed twin-boat.* This has an apparently untenable combination of bond angle, torsional, and

transannular strain. A Dreiding model is mechanically unstable with respect to (f).



SCHEME

(f) *The twin twist-boat.* This possesses a serious repulsion between the *endo*-hydrogen atoms on C-2 and C-6. There are additional, smaller interactions between C-3 and C-9, and C-7 and -10. Lateral distortion alleviates the C-2, C-6 interaction at the expense of angle

<sup>3</sup> (a) M. P. Doyle and W. Parker, *J.C.S. Perkin I*, in the press; preliminary report, M. P. Doyle and W. Parker, *Chem. Comm.*, 1970, 755; (b) R. S. Henry, W. T. Moodie, W. Parker, and C. I. F. Watt, *J.C.S. Perkin I*, 1975, 803.

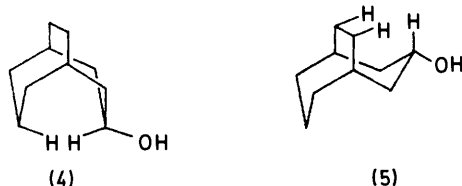
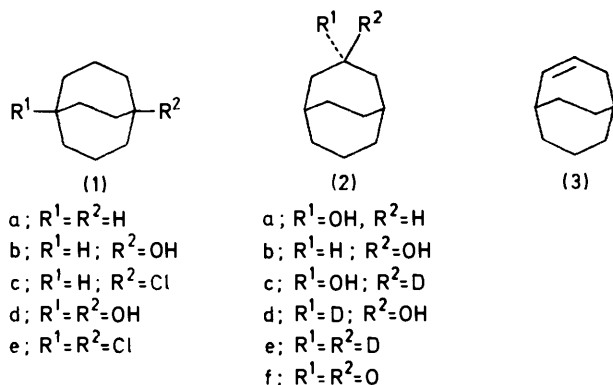
<sup>4</sup> (a) M. P. Doyle and W. Parker, *Chem. Comm.*, 1969, 319; (b) M. Doyle, R. Hafter, and W. Parker, *Tetrahedron Letters*, 1971, 3985.

<sup>1</sup> M. A. Eakin, J. Martin, and W. Parker, *Chem. Comm.*, 1968, 298; M. A. Eakin, J. Martin, W. Parker, Sister C. Egan (D.H.G.), and S. H. Graham, *ibid.*, p. 337.

<sup>2</sup> C. I. F. Watt and W. Parker, *J.C.S. Perkin II*, 1975, 1647.

strain and an increase in the other transannular interactions.

It is not immediately obvious which, if any, of these conformations is liable to be preferred, although we had found  $^1\text{H}$  n.m.r. evidence for a twin-chair conformation <sup>4a</sup> for bicyclo[3.3.2]decane-3-*exo*-ol (2a). The *exo*-configuration was inferred from the synthesis *via* hydroboration of bicyclo[3.3.2]dec-2-ene (3), a process known to occur from the less-hindered face of a double bond <sup>5</sup> which in this case is *exo* to the two-carbon bridge. Although this in no way constitutes a rigorous proof of stereochemistry, support comes from the  $^1\text{H}$  n.m.r. spectrum of (2a) in which the C-3 proton resonates at  $\tau$  5.7 as a strongly coupled multiplet. The magnitudes of the couplings (11 and 5 Hz) are only consistent with the proton being axial in a cycloheptane ring. The *exo*-configuration, and concurrently the twin-chair conformation (4) rather than the boat-chair alternative (5), is then established by the chemical shift of the H-3, which is appreciably deshielded \* relative to H-1 in cycloheptanol ( $\tau$  6.16). This effect must be transannular and stem therefore from the *endo* C-7 hydrogen atom in (4) or the *syn*-C-9 and C-10 positions in (5). In fact the extent of deshielding is similar to that found in the twin-chair bicyclo[3.3.1]nonan-3-*exo*-ol ( $\tau$  5.68) <sup>1</sup> and has to be contrasted with that for H-3 of bicyclo[3.2.1]octan-3-*exo*-ol <sup>7</sup> ( $\tau$  6.25) in which no transannular shielding is possible.

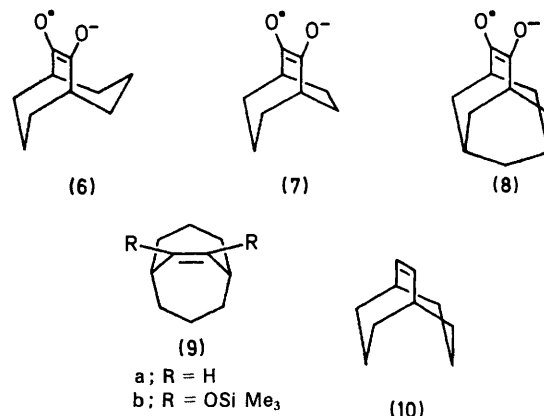


In contrast, Russell <sup>8</sup> has interpreted the e.s.r. spectra of bicyclo[3.3.2]decane-9,10-semidione (6) and bicyclo[3.2.2]nonane-6,7-semidione (7) as pointing to a preferred boat-chair conformation for (1a). He had previously

\* Large chemical shifts have been noted in the spectra of molecules suffering from serious steric compression, and have been ascribed to magnetic anisotropy of neighbouring C-H and C-C bonds and intramolecular van der Waals interactions. <sup>6</sup>

<sup>5</sup> H. C. Brown and G. Zweifel, *J. Amer. Chem. Soc.*, 1959, **81**, 247; 1961, **83**, 2544; 1964, **86**, 393; H. C. Brown, 'Hydroboration,' Benjamin, New York, 1962.

shown <sup>8b</sup> that, when a seven-membered ring is in a chair form,  $\beta$ -hydrogen atoms with *trans*-coplanar arrangements of bonds to the carbon  $p_z$  orbital of the  $\pi$ -system



have large hyperfine splitting (1.8–2.8 G), whereas when the ring in question is held in a boat form, such splittings are reduced to *ca.* 0.5 G. If (6) were to exist as a twin-chair, its e.s.r. spectrum would be similar to that of the homoadamantane semidione (8), which shows a quintet with four large splittings arising from the four equatorial  $\beta$ -hydrogen atoms. In the event, the spectrum of (6) was fully compatible with a boat-chair conformation for (6) and, by inference, for bicyclo[3.3.2]dec-9-ene (9a).

Russell then examined the bicyclo[3.2.2]nonane analogue (7) in order to ascertain the preference of saturated and unsaturated seven-membered rings for a chair conformation. At  $-65^\circ\text{C}$  an e.s.r. spectrum was obtained compatible with a conformation with the double bond in a chair arrangement. Relating this finding to those for bicyclo[3.3.2]decane-9,10-semidione (6) it was argued that here also one might expect to find a greater preference for a twin-chair arrangement than in the case of bicyclo[3.3.2]decane (1a) itself and since, in fact, (6) is shown to be a boat-chair then there is all the more reason for the hydrocarbon (1a) also to exist in this conformation. This argument is unsatisfactory. Any attempt to transpose the conformational preference of flexible molecular segments from one ring system to another without consideration of the entire molecule in question can frequently lead to erroneous conclusions.

<sup>6</sup> H. M. McConnell, *J. Chem. Phys.*, 1957, **27**, 226; C. Reid, *J. Mol. Spectroscopy*, 1957, **1**, 18; J. A. Pople, *Proc. Roy. Soc.*, 1957, **A**, **239**, 541, 550; G. Slomp and B. R. McGarvey, *J. Amer. Chem. Soc.*, 1959, **81**, 2200; A. D. Buckingham, *Canad. J. Chem.*, 1960, **38**, 310; N. Jonathan, S. Gordon, and B. P. Dailey, *J. Chem. Phys.*, 1962, **36**, 2443; R. J. Abraham and J. S. E. Holker, *J. Chem. Soc.*, 1963, 806; T. Schaeffer, W. F. Reynolds, and Y. Youmemoto, *Canad. J. Chem.*, 1963, **41**, 2969; W. Nagata, T. Terasawa and K. Tori, *J. Amer. Chem. Soc.*, 1968, **86**, 3746; D. R. Arnold, D. T. Trecker, and E. B. Whipple, *ibid.*, 1965, **87**, 2596; S. Winstein, P. Carter, F. A. L. Anet, and A. J. R. Bourn, *ibid.*, 5247; M. A. Battiste and M. E. Brennan, *Tetrahedron Letters*, 1966, 5857; T. B. Cobb and J. D. Memory, *J. Chem. Phys.*, 1967, **47**, 2020; B. V. Cheney, *J. Amer. Chem. Soc.*, 1968, **90**, 5386; J. Haywood-Farmer, H. Malkins, and M. A. Battiste, *ibid.*, 1972, **94**, 2209.

<sup>7</sup> C. W. Jefford, J. Gunsher, and B. Waegell, *Tetrahedron Letters*, 1962, 741.

<sup>8</sup> G. A. Russell and R. G. Keske, *J. Amer. Chem. Soc.*, 1970, **92**, (a) p. 4458; (b) p. 4460.

Indeed a Dreiding model of the 9-ene (9a) shows clearly that the double bond markedly restricts the flexibility of the entire molecule by fixing the coplanarity of C-1, C-9, C-10, and C-5 while in a twin-chair conformation (10), greatly increasing the interaction between C-3 and C-7. On the other hand, in a boat-chair conformation the interaction of C-9 and C-10 with C-3 is much reduced, as compared with the corresponding situation in bicyclo[3.3.2]decane. Thus, it is not at all unreasonable that whereas 9-ene derivatives may prefer a boat-chair conformation, those derivatives with a saturated two-carbon bridge may yet prefer a twin-chair arrangement.

High frequency methylene stretching  $\nu(\text{CH})^9$  and scissoring  $\delta(\text{CH})$  bands have been noted in the i.r. spectra of compounds whose molecular geometry is characterised by severe steric congestion, and the presence of such bands in spectra both of the solid state and of solutions, coupled with X-ray crystallographic analysis, has been used to establish the preferred conformation of the closely related bicyclo[3.3.1]nonane<sup>11</sup> (11) and tricyclo[5.3.1.1<sup>2,6</sup>]dodecane<sup>12</sup> (12) as laterally distorted twin-chairs in which the two ends of the molecule are splayed apart to relieve the strong C-3,C-7 interaction.<sup>13</sup> With these analogies to hand, we sought to apply these techniques to the current conformational problem.

Table I shows the relevant spectral data \* for a series of bicyclo[3.3.2]decanes prepared in the course of this and related<sup>3,15</sup> investigations, and it is clear that



the appearance of high frequency stretching and scissoring absorption bands is dependent on the nature and

\* The  $\nu(\text{CH})$  region of these spectra is complex giving, in the main, only a broad band envelope even with a high resolution grating spectrophotometer. Consequently the only high frequency band which can be discerned is that due to the larger frequency shift in the symmetric-antisymmetric, less intense  $\nu_0$  mode. In addition, since the frequency shifts in this series of compounds are uniformly smaller than those found in rigid caged molecules,<sup>9a,b</sup> these bands are usually visible as shoulders on the high frequency side of the main absorption envelope. On the other hand the high frequency  $\delta(\text{CH})$  scissoring absorptions are usually much better resolved (*cf.* ref. 11).

<sup>9</sup> (a) L. deVries and P. R. Ryason, *J. Org. Chem.*, 1961, **26**, 621; (b) D. Kivelson, S. Winstein, P. Bruck, and R. L. Hansen, *J. Amer. Chem. Soc.*, 1961, **83**, 2938.

<sup>10</sup> (a) G. Chiurdoglu, Th. Doehaerd, and B. Tursch, *Bull. Soc. chim. France*, 1960, **69**, 1322; *Chem. and Ind.*, 1959, **9**, 1453; (b) J. Dale, I. Laszlo, and W. Ruland, *Proc. Chem. Soc.*, 1964, 190.

<sup>11</sup> J. Martin, Ph.D. Thesis, University of Glasgow, 1964; G. Eglinton, J. Martin, and W. Parker, *J. Chem. Soc.*, 1965, 1243; M. Stoll, B. Willhalm, and G. Büchi, *Helv. Chim. Acta*, 1955, **38**, 1573; W. A. C. Brown, G. Eglinton, J. Martin, W. Parker, and G. A. Sim, *Proc. Chem. Soc.*, 1964, 57; W. A. C. Brown, J. Martin, and G. A. Sim, *J. Chem. Soc. (C)*, 1965, 1844. See also N. C. Webb and M. R. Becker, *ibid.*, 1967, 1317; M. Dobler and J. D. Dunitz, *Helv. Chim. Acta*, 1964, **47**, 695; N. W. J. Pumphrey and M. J. T. Robinson, *Chem. and Ind.*, 1963, 1903; I.U.P.A.C. Congress, London, 1963, Abstracts A3-A19, p. 135; N. W. J. Pumphrey, Ph.D. Thesis, Liverpool University, 1965.

location of functionality on the [3.3.2] carbon skeleton as is the case in the bicyclo[3.3.1]nonane system.<sup>11</sup> With the exception of the *exo*- and *endo*-3-ols (see later) these bands are *present* whenever both three-carbon bridges

TABLE I

Abnormal i.r.  $\delta(\text{CH})$  and  $\nu(\text{CH})$  absorptions ( $\text{cm}^{-1}$ ) of various bicyclo[3.3.2]decanes (normal bands not listed)

(1a)	1 489	2 980	(16)	1 485	2 990
(1b)	1 493	2 989sh	(18)	1 485	2 990
(1c)	1 493	2 983			
(1d) (solid)	1 485	2 979	(19)		
(1d) (soln.)		2 982	(20a)		
(1e)	1 485	2 982sh	(20b)		
			(20c)		
(2a)			(21a)		
(2b)			(21b)		
(2c)			(21c)		
(2d)					
(2e)			(22a)	1 480	2 955
				(low)	
			(22b)		
(2f)			(22c)	1 485sh	2 900
(3)			(22d)		
(9a)	1 485 *		(22e)		
(9b)					
(13)			(23)		
(14)			(24a)		
			(24b)		
(15a)	1 483	2 920	(24c)		
(15b)	1 486	2 940	(25a)		
(15c)	1 485	2 920	(25b)		

are propano in nature, *e.g.* (1a—e), (15a—c), and (22a). This is so even for the 9,10-dione (16) and the lactone (18) in which there can be no methylene interactions involving the three- and two-carbon bridges and where one might have imagined that the adoption of a boat-chair or boat-boat conformation would be more favoured than in any of the other derivatives. In this context

<sup>12</sup> G. Ferguson, W. D. K. Macrossan, J. Martin, and W. Parker, *Chem. Comm.*, 1967, 102; W. D. K. Macrossan and G. Ferguson, *J. Chem. Soc. (B)*, 1968, 242.

<sup>13</sup> For related work see E. J. Corey and E. Block, *J. Org. Chem.*, 1966, **31**, 1663; E. D. Weill, K. J. Smith, and J. R. Gruber, *ibid.*, p. 1669; H. S. Aaron, C. P. Ferguson, and C. P. Rader, *J. Amer. Chem. Soc.*, 1967, **89**, 1431; J. P. Schaeffer, J. C. Lark, C. A. Flegal, and L. M. Honig, *J. Org. Chem.*, 1967, **32**, 1372; R. Lygo, J. McKenna, and I. O. Sutherland, *Chem. Comm.*, 1965, 356; E. N. Marvell and S. Provant, *J. Org. Chem.*, 1964, **29**, 3084; E. N. Marvell, G. J. Gleicher, D. Sturmer, and K. Salisbury, *ibid.*, 1968, **33**, 3393; J. E. Douglass and T. B. Ratliff, *ibid.*, 355; J. M. McEuen, R. P. Nelson, and R. G. Lawton, *ibid.*, 1970, **35**, 690; M. R. Chakrabarty, R. L. Ellis, and J. L. Roberts, *ibid.*, 1970, **35**, 541; J. N. Labows and D. Swern, *ibid.*, 1972, **37**, 3004; W. D. Macrossan, J. Martin, and W. Parker, *Tetrahedron Letters*, 1965, 2589; C.-Y. Chen and R. J. W. LeFevre, *J. Chem. Soc. (B)*, 1966, 539; L. A. Paquette and J. W. Heilmaster, *J. Amer. Chem. Soc.*, 1966, **88**, 763; S. Danishefsky, W. E. Hatch, M. Sax, E. Abola, and J. Pletcher, *ibid.*, 1973, **95**, 2410; M. Fisch, S. Smallcombe, J. C. Gramain, M. A. McKerver, and J. E. Anderson, *J. Org. Chem.*, 1970, **35**, 1886; M. R. Vegar and R. J. Wells, *Tetrahedron Letters*, 1971, 2847; J. A. Peters, J. D. Remijnse, A. van der Wiele, and H. van Bekkum, *ibid.*, p. 3065; I. Fleming, S. W. Hanson, and J. K. M. Sanders, *ibid.*, p. 3733; B. J. Calvert and J. D. Hobson, *J. Chem. Soc.*, 1964, 5378; C. Tamura and G. A. Sim, *J. Chem. Soc. (B)*, 1968, 1241; P. D. Cradwick and G. A. Sim, *ibid.*, 1971, 2218; and ref. 14.

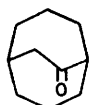
<sup>14</sup> E. M. Engler, J. D. Andose, and P. von R. Schleyer, *J. Amer. Chem. Soc.*, 1973, **95**, 8005.

<sup>15</sup> R. Hafter and W. Parker, *J.C.S. Perkin I*, submitted for publication.

it is notable that the i.r. spectrum of homoadamantane shows no significant abnormal bands. Hence these



(13)

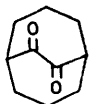


(14)

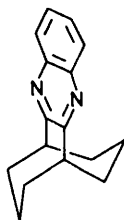


(15)

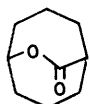
- a:  $R^1 = \text{OH}, R^2 = \text{H}$   
 b:  $R^1 = \text{OAc}, R^2 = \text{H}$   
 c:  $R^1 R^2 = \text{O}$



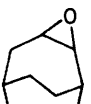
(16)



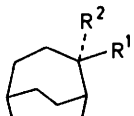
(17)



(18)

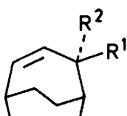


(19)



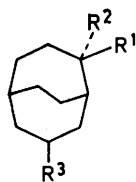
(20)

- a:  $R^1 = \text{OH}, R^2 = \text{H}$   
 b:  $R^1 = \text{OAc}, R^2 = \text{H}$   
 c:  $R^1 R^2 = \text{O}$



(21)

- a:  $R^1 = \text{OH}, R^2 = \text{H}$   
 b:  $R^1 = \text{OAc}, R^2 = \text{H}$   
 c:  $R^1 R^2 = \text{O}$

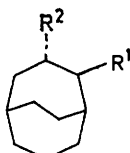


(22)

- a:  $R^1 = \text{OH}, R^2 = \text{H}, R^3 = \text{H}$   
 b:  $R^1 R^2 = \text{O}, R^3 = \text{H}$   
 c:  $R^1 = R^2 = \text{D}, R^3 = \text{H}$   
 d:  $R^1 = \text{OH}, R^2 = \text{H}, R^3 = \text{OH}$   
 e:  $R^1 = \text{OAc}, R^2 = \text{H}, R^3 = \text{OAc}$

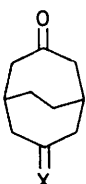


(23)



(24)

- a:  $R^1 = \text{OH}, R^2 = \text{D}$   
 b:  $R^1 = \text{OH}, R^2 = \text{OH}$   
 c:  $R^1 = \text{OAc}, R^2 = \text{OAc}$



(25)

- a:  $X = \text{CH}_2$   
 b:  $X = \text{O}$

(14), (20a—c), (21a—c), and (23)] or an epoxide (19) lead to the initial conclusion that the high frequency absorptions have their origin in transannular interaction between the methylene groups of the propano bridges, *i.e.* either C-3,C-7 in the twin-chair conformers (a) and (b) and/or C-3,C-6,C-8 in the boat-chair forms (c) and (d) and/or C-2,C-6 and C-4,C-8 in the twin-boat forms (f) and (e). Further, the absence of such  $\delta(\text{CH})$  and  $\nu(\text{CH})$  bands in the spectra of the 3,3-dideuteriohydrocarbon (2e) (*cf.* ref. 10b) and the alcohols (2a—d) serves to pinpoint the C-3 methylene group as one of the participants. On the other hand, 2,2-dideuteriobicyclo[3.3.2]decane (22c) and the *exo*-2-ol (22a) do show these absorptions, albeit of weaker intensity, and this leads to the conclusion that these spectral characteristics arise from C-3,C-7 methylene interaction in a twin-chair conformation (a) or (b).

Martin<sup>11</sup> has obtained a reasonable separation-frequency relationship by estimating, from molecular models, the distance between the opposed hydrogen atoms in a group of rigid fused-ring compounds which show abnormal  $\nu(\text{CH})$  bands. This, in turn, led him to estimate the distance between the *endo*-hydrogen atoms on C-3 and C-7 in the twin-chair bicyclo[3.3.1]nonane (11) as 170 pm, in close agreement with the subsequent X-ray-derived<sup>18</sup> value (180 pm). From the data in Table 1, the corresponding distance in bicyclo[3.3.2]decane can be calculated as 200 ( $\pm 20$ ) pm, in contrast with Dreiding models which suggest a smaller interhydrogen distance for (1a) than (11). The obvious conclusion is that the two-carbon bridge markedly increases the flexibility in the bicyclodecane system, an important factor to be borne in mind when analysing its chemical reactivity.

The 9-ene (9a) and the structurally related quinoxaline (17) are predicted to exist preferentially in a boat-chair conformation (see later) and indeed neither exhibited a band at 2980  $\text{cm}^{-1}$ . While the region immediately below 1500  $\text{cm}^{-1}$  is obscured by strong aromatic bending absorption in the case of (17), the simple olefin (9a) shows a very weak shoulder at 1485  $\text{cm}^{-1}$  in spectra of very concentrated solutions, although this absorption is absent in solid state spectra. It is possible that this is the result of a heavily biased boat-chair-twin-chair equilibrium in concentrated solutions of the 9-ene, a small quantity of the twin-chair conformer being responsible for the weak high frequency scissoring band. An X-ray crystallographic analysis of the quinoxaline (17) has been completed ( $R = 0.055$ ) in these laboratories.<sup>16</sup> The molecule is in the expected boat-chair conformation and has almost exact  $C_s$  symmetry. The bond lengths are all within expected limits and the angles in the aromatic moiety are normal. As twisting is virtually impossible in this molecule, strain in the bridged system is relieved by bond and torsional angle distortion; thus the average value for the methylene

facts and the absence of such bands when one or both three-carbon bridges contain a double bond [*e.g.* (13),

<sup>16</sup> (a) R. Hafter, J. Murray-Rust, P. Murray-Rust, and W. Parker, *J.C.S. Chem. Comm.*, 1972, 1127; (b) J. Murray-Rust and P. Murray-Rust, *Acta Cryst.*, 1975, **B31**, 310.

bond angle is  $116.2(2)^\circ$  and the angles at the bridgehead are in the range  $112.2$ – $112.9^\circ$ . The torsion angles also vary by up to  $15^\circ$  from those predicted from a strain-free model. The most obvious cause of the molecular distortion is the non-bonded repulsions between the indicated hydrogen atoms, and is clearly reflected in the dihedral angles C-2,C-3,C-4/C-1,C-2,C-4,C-5 and C-6,C-7,C-8/C-1,C-5,C-6,C-8 ( $53.0$  and  $51.1^\circ$ ) respectively; *cf. ca.*  $66^\circ$  estimated from models.

We are currently engaged in the X-ray crystallographic analysis of a group of bridgehead-substituted bicyclo[3.3.2]decanes which exhibit abnormal (CH) absorptions both in solution and in the solid state. Unfortunately, the 1-ol (1b) has a disordered crystal structure and the structure of the diol (1d), being tetragonal is difficult to solve by direct methods. However we shall report on the detailed structure of this compound and the dichloride (1e) in the near future.

At this stage it is relevant to consider the application of force-field calculations to the various conformations (Scheme) of bicyclo[3.3.2]decane. Schleyer and his co-workers<sup>17</sup> find that both the boat-chair and twin-boat conformation show broad energy minima, *i.e.* there is no significant energy difference between the eclipsed boat-chair (d) and the one with a fully staggered bridge (c), and so also for (e) as compared with (f). On the other hand (a), with a staggered two-carbon bridge of dihedral angle  $22^\circ$ , is claimed to be *ca.*  $2.4$  kcal mol<sup>-1</sup> more stable than the eclipsed form (b). In addition the boat-chair (c) and (d) and twin twist-chair (a) forms are calculated to be of equal energy and *ca.*  $2.5$  kcal mol<sup>-1</sup> more stable than the twin-boat conformers (e) and (f).†

To date there are two pieces of experimental data to place beside these molecular mechanics calculations. First, our experimentally determined<sup>19</sup> gas phase enthalpy of formation [ $-\Delta H_f^\circ(g)$ ] of the hydrocarbon ( $25.3 \pm 1.8$  kcal mol<sup>-1</sup>) agrees well with the figures calculated<sup>14</sup> by employing either Allinger ( $25.20$  kcal mol<sup>-1</sup>) or Schleyer ( $26.17$  kcal mol<sup>-1</sup>) force fields. Secondly, the reductions with sodium-moist ether of bicyclo[3.3.2]decan-3-one (2f) is a thermodynamically controlled process and the experimental ratio of *exo*- to *endo*-3-ols ( $0.92 : 1$ ) reflects the virtual equal energy content of the twin-chair and boat chair conformations, at least as far as those with a chair-equatorial or boat-equatorial 3-hydroxy-substituent are concerned.

With this information to hand, the possibility of the bicyclo[3.3.2]decane skeleton existing in solution as a finely balanced boat-chair-chair equilibrium can-

† This paper employs a less well refined<sup>18</sup> force field, *e.g.* the calculated  $\Delta H_f^\circ$  values (kcal mol<sup>-1</sup>; gas phase;  $25^\circ\text{C}$ ) for the various conformations of bicyclo[3.3.2]decane and homoadamantane within the ethano-bridge torsional angle noted are as follows: bicyclo[3.3.2]decane, boat-chair  $-32.8 (\pm 18^\circ)$ ; boat-boat  $-30.1 (\pm 15^\circ)$ ; chair-chair  $-32.3 (22^\circ)$ ;  $-30.0 (0^\circ)$ ; homoadamantane  $-34.5 (\pm 33^\circ)$ . These figures have to be compared with those quoted for bicyclo[3.3.2]decane [(a)  $-25.20$ ; (b)  $-26.17$ ] and homoadamantane [(a)  $-29.96$ ; (b)  $-27.77$ ] in a more recent publication<sup>14</sup> from the Princeton laboratories [(a) refers to Schleyer-Engler force field and (b) to Allinger force field].

not be ruled out, and although the <sup>1</sup>H n.m.r. spectrum of (2a) shows no signal for a normal CH-OH (*i.e.* a boat cycloheptane-chair cycloheptanol conformer) there is some i.r. evidence that this may be the case. Table 2

TABLE 2

Abnormal  $\delta(\text{CH})$  maxima and extinction coefficients for a series of bicyclo[3.3.2]decanes and bicyclo[3.3.1]nonanes in carbon tetrachloride solution

Compound	$\delta(\text{CH})$	$\epsilon_\delta$	Conc. (M)
(15a)	1 486	22 <sup>a</sup>	0.065
(1a)	1 485	13 <sup>a</sup>	0.362
(15c)	1 485	6.5 <sup>a</sup>	0.129
(16)	1 485	4 <sup>a,*</sup>	0.018
(9a)	1 485 (sh)	2 <sup>a,*</sup>	0.067 5
1,5-Dimethylbicyclo[3.3.1]nonane	1 488	20 <sup>b</sup>	0.05
1,5-Dimethylbicyclo[3.3.1]nonan-9-ol	1 490	45 <sup>b</sup>	0.05
1,5-Dimethylbicyclo[3.3.1]nonan-9-one	1 490	45 <sup>b</sup>	0.05
1,5-Dimethylbicyclo[3.3.1]non-2- <i>exo</i> -ol	1 488	45 <sup>c</sup>	0.001

<sup>a</sup> 1 mm cell. <sup>b</sup> 0.51 mm cell. <sup>c</sup> 2 cm cell.

\* Weak band,  $\epsilon$  approximate.

lists the extinction coefficients of the abnormal  $\delta(\text{CH})$  bands for some of the compounds mentioned in Table 1 along with a related group of bicyclo[3.3.1]nonanes. The extinction coefficients of all the bridgehead-substituted compounds (1b–e) are similar and the frequency is almost constant, but the intensity is dependent on the steric requirement of the two-carbon bridge: 9-ol (15a) > hydrocarbon (1a) > 9-one (15c) > 9,10-dione > 9-ene (9a). Winstein<sup>9b</sup> has suggested that only the frequency of the abnormal  $\nu(\text{CH})$  bonds is affected by the interhydrogen distance whenever the intensity is largely governed by the strength of the coupling between the interacting methylene groups. If this argument also holds for the  $\delta(\text{CH})$  absorptions, the observed intensity differences cannot be due to increased splaying apart of the two rings of a twin-chair conformation facilitated by a decreased steric requirement of the two-carbon bridge. The most likely explanation is that, as the steric demands of the two-carbon bridge diminish, the proportion of boat-chair conformer increases and so the abnormal band intensity decreases. The abnormal  $\delta(\text{CH})$  bands observed for the bicyclo[3.3.2]decane system are uniformly weaker than those in the bicyclo[3.3.1]nonane<sup>11</sup> system, where the twin-chair conformer is strongly preferred.<sup>11,13</sup>

If the above argument is valid, we have a method for determining the proportion of twin-chair conformer in solution, given that there are available the requisite data for a locked twin-chair form. Synthetic work with

<sup>17</sup> E. M. Engler, L. Chang, and P. von R. Schleyer, *Tetrahedron Letters*, 1972, 2525.

<sup>18</sup> G. J. Gleicher and P. von R. Schleyer, *J. Amer. Chem. Soc.*, 1967, **89**, 582; R. C. Bingham and P. von R. Schleyer, *ibid.*, 1971, **93**, 3189.

<sup>19</sup> W. Parker, W. V. Steele, and C. I. F. Watt, *J. Chem. Thermodynamics*, 1977, **9**, 87.

this aim is in hand \* but in the meantime we can report the appearance of strong abnormal  $\delta(\text{CH})$  and  $\nu(\text{CH})$  bands at 2 990 and 1 489  $\text{cm}^{-1}$  in the i.r. spectrum of 9,10-bis(trimethylsilyloxy)bicyclo[3.3.2]dec-9-ene (9b), where the bulky trimethylsilyloxy-groups prevent the bicyclo[3.3.2]decene framework adopting its preferred boat-chair arrangement and cause a transition to the fully eclipsed twin-chair form.

Turning to the question of whether the ethano-bridge in bicyclo[3.3.2]decane is eclipsed or staggered, we note the techniques which have been applied to homoadamantane (26a) where the same problem pertains. Both Schleyer<sup>21</sup> and Nordlander<sup>22</sup> have commented that the carbonyl stretching frequency (1 698  $\text{cm}^{-1}$ ) of 4-homoadamantanone (26b) is much more compatible with an eclipsed than with a staggered two-carbon bridge.<sup>23</sup> In the same paper Schleyer has presented evidence for an eclipsed bridge in the form of the solution i.r. spectrum of *cis*-homoadamantane-4,5-diol (27), which shows a large intramolecular hydrogen bond frequency shift ( $\Delta\nu$  89  $\text{cm}^{-1}$ ), suggesting that this possesses a small dihedral angle and hence the preferred conformation of (26a) is itself eclipsed. However it should be realised that the gain in energy resulting from an intramolecular hydrogen bond can often be <sup>24a</sup> *ca.* 5 kcal  $\text{mol}^{-1}$  and consequently may exert considerable control over the adoption of a particular conformation. Indeed, in a later paper,<sup>24b</sup> the Princeton group have highlighted cases in which there is a breakdown in the OH  $\cdots$  OH spectral shift-dihedral angle relationship. Leonard and Mader<sup>25</sup> have noticed a relationship between the u.v.  $\lambda_{\text{max}}$  of non-enolisable  $\alpha$ -diketones and the dihedral angle between the planes of the carbonyl groups as estimated from molecular models, and Schlatmann<sup>26</sup> has interpreted the  $\lambda_{\text{max}}$  value (418 nm) of homoadamantane-4,5-dione (26c) (which has been shown by X-ray analysis<sup>27</sup> to correspond to a dihedral angle of 11.9°) as evidence for an almost fully eclipsed bridge in the parent hydrocarbon on the grounds that the vicinal nature of the two carbonyl groups should give rise to a strong dipole-dipole repulsion. Hence, unless there is a conformational force constraining the two carbonyl groups to a virtually eclipsed conformation, the dihedral angle should be considerably larger than 11.9°.

The Princeton group<sup>28</sup> have analysed the 220 MHz <sup>1</sup>H n.m.r. spectrum of (26a) and found it to be tempera-

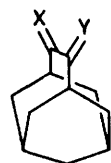
\* While *trans*-9,10-dimethylbicyclo[3.3.2]decane is probably the most suitable compound, the steric requirements of the corresponding *trans*-9,10-dibromide should be as great. However initial attempts to prepare it from the 9-ene (9a) result in the uptake of more than one equivalent of reagent, presumably owing to bridgehead (allylic) halogenation (see ref. 20 and refs. quoted therein for related cases of susceptibility to bridgehead free-radical substitution).

<sup>20</sup> For n.m.r. data for the corresponding bicyclo[3.3.1]nona-2,6-diene see *e.g.* H. Stetter and F. F. Schwarz, *Chem. Ber.*, 1968, **101**, 2464; (b) M. J. Goldstein, S. Tomoda, and G. Whittaker, *J. Amer. Chem. Soc.*, 1974, **96**, 3676.

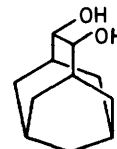
<sup>21</sup> P. von R. Schleyer, E. Funke, and S. Liggero, *J. Amer. Chem. Soc.*, 1970, **91**, 3965.

<sup>22</sup> J. E. Nordlander, F. Ying-Hsieh Wu Satya, P. Jindal, and J. B. Hamilton, *J. Amer. Chem. Soc.*, 1970, **91**, 3962.

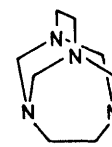
ture independent. The protons of the ethano bridge are reported to correspond to the  $A_4$  portion of a  $A_4X_2$  system ( $J_{\text{AX}}$  1.8 Hz) which indicates a dihedral angle of *ca.* 60° between the bridgehead proton and the bridge



(26)



(27)



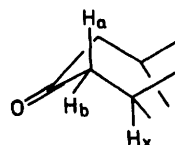
(28)

a; X = H<sub>2</sub>, Y = H<sub>2</sub>

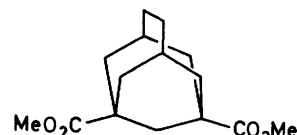
b; X = H<sub>2</sub>, Y = O

c; X = O, Y = O

methylene, corresponding in turn to an eclipsed conformation for homoadamantane. On the other hand, although an early strain energy calculation<sup>18</sup> supported this view, a later analysis using a more refined force and energy surface search<sup>17</sup> has revealed a very broad energy minimum over >30° torsional angle range (C-CH<sub>2</sub>-CH<sub>2</sub>-C), indicating that there is effectively no energy difference between a staggered ( $C_2$ ) and a fully eclipsed ( $C_{2v}$ ) bridge, (see footnote \*). In this context the X-ray crystallographic studies of Murray-Rust and his co-workers are particularly revealing. They had previously shown that the tetra-aza-system (28)<sup>29</sup> in the crystal adopts a conformation with planar ethano-bridges but with pronounced vibration perpendicular to the plane of the bridge, and very recently they have completed the analysis of the 1,8-bismethoxycarbonyl derivative (29).<sup>30</sup> The structure consists of discrete



(30)



(29)

molecules with no unusually short intermolecular contact distances and so it is reasonable to assume that the observed configuration is close to that of minimum energy. The homoadamantane nucleus has almost  $C_{2v}$  symmetry and the torsional angle in the ethano-bridge is 2.0(6)°. The thermal ellipsoids of C-4 and C-5

<sup>23</sup> J. O. Halford, *J. Chem. Phys.*, 1956, **24**, 830; D. Cook, *Canad. J. Chem.*, 1961, **39**, 31; J. I. Brauman and V. W. Laurie, *Tetrahedron*, 1968, **24**, 2595.

<sup>24</sup> (a) E. S. Gould, 'Mechanism and Structure in Organic Chemistry,' Holt-Rinehart-Winston, New York, 1959, p. 29; (b) T. M. Gorrie, E. M. Engler, R. C. Bingham, and P. von R. Schleyer, *Tetrahedron Letters*, 1972, 3039.

<sup>25</sup> N. J. Leonard and P. M. Mader, *J. Amer. Chem. Soc.*, 1950, **72**, 5388.

<sup>26</sup> J. L. M. A. Schlatmann, J. G. Korsloot, and J. Schut, *Tetrahedron*, 1970, **26**, 949.

<sup>27</sup> P. B. Braun, J. Hornstra, and J. I. Leenhouts, *Acta Cryst.*, 1970, **B26**, 1802.

<sup>28</sup> S. H. Liggero, P. von R. Schleyer, and K. C. Ramey, *Spectroscopy Letters*, 1969, **2**, 197.

<sup>29</sup> P. Murray-Rust, *J.C.S. Perkin II*, 1974, 1136.

<sup>30</sup> J. Murray-Rust, P. Murray-Rust, and R. S. Henry, *Acta Cryst.*, 1975, **B31**, 585.

do not show any unusual anisotropic motion perpendicular to the bridge; indeed the ester group vibration is more pronounced.

Hence the weight of evidence points to the  $C_{2v}$  conformation of homoadamantane being more stable than the  $C_2$  arrangements, and to date the corresponding evidence for bicyclo[3.3.2]decane points in the same direction, *e.g.* the 9-one (15c) exhibits a carbonyl stretching frequency at  $1\ 697\text{ cm}^{-1}$ , more in agreement with an eclipsed bridge and a C-CO-C bond angle of  $127^\circ$ . In addition, the C-10 protons in this compound are magnetically equivalent, resonating at  $\tau\ 7.46$  as a sharp doublet ( $J_{AX}\ 6\text{ Hz}$ ). Thus the ethano-bridge is either eclipsed or in a rapid conformational equilibrium between the two staggered forms. The u.v.  $\lambda_{\text{max}}$  value of the 9,10-dione (16) (421 nm) is very close to that of homoadamantanedione, suggesting that the dihedral angle in (16) can be only marginally larger than that in (26c), and consequently favouring an eclipsed bridge. However there is some i.r. evidence for a boat-chair  $\rightleftharpoons$  twin chair equilibrium in (16) and the recorded  $\lambda_{\text{max}}$  value could well be affected by molecules in the former arrangement.

The ground-state conformation of the 3-one (2f) is of particular interest to us in view of our interest in solvolytic reactivity at this position. The insertion of an  $sp^2$  centre at C-3 removes many of the steric interactions present in (1a) and the 220 MHz  $^1\text{H}$  n.m.r. spectrum of (2f) is most informative. The protons at C-2 and C-4 are only coupled to the bridgehead hydrogen atoms and form the AB part of an ABX (or rather two equivalent ABX) systems,  $J_{AB}\ 17$ ,  $J_{AX}\ 3$ ,  $J_{BX}\ 5\text{ Hz}$ , where  $H_A$  and  $H_B$  are the axial and equatorial protons, respectively. Vicinal couplings of 3 and 5 Hz can best be accounted for if the cycloheptanone is in a chair form with the bridgehead proton ( $H_X$ ) virtually bisecting the angle between the  $\alpha$ -methylene protons (30). Further it is possible to come to some conclusion about the relative orientation of the carbonyl group and the  $\alpha$ -methylene protons from the magnitude of the geminal coupling ( $J_{AB}\ 17\text{ Hz}$ ). The geminal coupling constants of a large number of substituted cycloheptanes have been examined by Schmid<sup>31</sup> and found to be fairly constant at  $-13.5$  to  $-14\text{ Hz}$ . Barfield and Grant<sup>32</sup> have analysed the effect of an adjacent  $\pi$ -bonded system on these geminal couplings and found a contribution which varies from 0 to  $-4\text{ Hz}$ , depending on the dihedral angle between the methylene group and the adjacent  $\pi$ -bond. Thus, if we assume a negative geminal coupling constant for (2f), there appears to be a  $\pi$ -contribution of  $-3$  to  $-3.5\text{ Hz}$  which corresponds to a dihedral angle of  $45$ – $50^\circ$  as compared with  $75$ – $80^\circ$  taken from molecular models, *i.e.* the cycloheptanone is splayed outwards by about  $30^\circ$ , producing considerable angle strain, which is itself manifest in the associated i.r. carbonyl stretching fre-

quency of  $1\ 692\text{ cm}^{-1}$ , equivalent to a C-CO-C bond angle of  $132.5^\circ$ .

#### EXPERIMENTAL

M.p.s were determined for samples in sealed capillary tubes heated in an aluminium block. Mass spectra were determined by the Physico-chemical Measurements Unit at Aldermaston (A.E.I. MS9 spectrometer). U.v. absorption spectra were recorded for solutions in ethanol with a Unicam SP 800 spectrophotometer. Routine i.r. spectra were determined for solutions in carbon tetrachloride (unless stated otherwise) with a Perkin-Elmer 157G or 457 spectrophotometer. High resolution i.r. spectra were recorded for solutions in carbon tetrachloride with Perkin-Elmer 521 and 225 spectrophotometers. Routine n.m.r. spectra were measured for solutions in carbon tetrachloride (unless otherwise stated) with a Perkin-Elmer R10 (60 MHz) spectrometer ( $\text{Me}_4\text{Si}$  as internal reference). High resolution n.m.r. spectra were recorded by the P.C.M.U. [Varian HA 100 (100 MHz) and HR 220 (220 MHz) spectrometers]. Microanalyses were carried out at Oxford by Dr. F. B. Strauss and his staff. Analytical g.l.c. was carried out with a Perkin-Elmer F11 instrument. Preparative g.l.c. was performed on a Varian Aerograph 700 instrument. Light petroleum refers to the fraction of b.p.  $40$ – $60^\circ\text{C}$ . Organic extracts were dried over anhydrous magnesium sulphate unless otherwise stated. Alumina for chromatography was Laporte type H, deactivated with 5% (w/w) water, unless stated otherwise. All compounds containing the bicyclo[3.3.2]decane ring system were treated as if they were both volatile and unstable in air, *i.e.* they were always stored in sealed containers under nitrogen at  $-20^\circ\text{C}$ .

*Bicyclo[3.3.2]decane* (1a).—Bicyclo[3.3.2]decan-9-one (10 g) and hydrazine hydrate (100%; 4.2 ml) were added to a solution of sodium (3.5 g) in diethylene glycol (160 ml). The mixture was then warmed for 1 h, and then heated under reflux for a further hour during which time the product sublimed into the condenser. The cooled mixture was then diluted with water (250 ml) and thoroughly extracted with *n*-pentane ( $3 \times 50\text{ ml}$ ). The sublimate was also dissolved in pentane and the combined organic extracts were then washed twice with water and dried. Fractional distillation gave a waxy solid which was purified by vacuum sublimation to give the hydrocarbon (1a) (7.9 g, 89%) m.p.  $177$ – $179^\circ$  (lit.,<sup>33</sup>  $177$ – $178$ ; lit.,<sup>34</sup>  $179$ – $181$ ; lit.,<sup>35</sup>  $164$ – $165^\circ$ );  $\nu_{\text{max}}$  2 990sh, 2 918, 2 865, 1 485, 1 465, and  $1\ 450\text{ cm}^{-1}$ ,  $\tau(\text{CCl}_4)$  7.8br (2 H), 8.22, 8.25, and 8.28 (4 H), and 8.35 (12 H).

*Bicyclo[3.3.2]decan-1-ol* (1b).—Chromium trioxide (1.6 g) was added in portions to a stirred solution of (1a) (1.0 g) in acetic acid (15 ml) and acetic anhydride (15 ml) over 1 h, the temperature being held below  $30^\circ\text{C}$ . After a further 30 min the mixture was poured onto ice and thoroughly extracted with ether ( $3 \times 50\text{ ml}$ ). The combined extracts were washed with saturated sodium hydrogen carbonate solution and then dried. Lithium aluminium hydride (100 mg) was then added, the mixture was stirred for 2 h, and the excess of hydride was destroyed by cautious addition of water. The inorganic salts were filtered off and the solvent was removed by distillation to give the crude

<sup>31</sup> S. Kabus, H. Friebolin, and H. Schmid, *Tetrahedron Letters*, 1965, 469.

<sup>32</sup> M. Barfield and D. M. Grant, *J. Amer. Chem. Soc.*, 1963, **85**, 1899.

<sup>33</sup> G. Schroeder, *Angew. Chem. Internat. Edn.*, 1963, **2**, 481.

<sup>34</sup> R. C. Bingham and P. von R. Schleyer, *J. Org. Chem.*, 1971, **36**, 1198.

<sup>35</sup> K. Alder, S. Hartung, and G. Hausmann, *Chem. Ber.*, 1956, **89**, 1972.

alcohol, which was absorbed on alumina from light petroleum. Elution with ether–light petroleum (1 : 1) furnished the 1-ol (450 mg, 40%) which was further purified by vacuum sublimation to give a crystalline solid, m.p. 193–198° (lit.,<sup>34</sup> 191–194°),  $\nu_{\max}$ . 3 612, 2 989sh, 2 929, 2 870, 1 486, 1 465, 1 454, 1 074, 996, 924, and 875  $\text{cm}^{-1}$ ,  $\tau(\text{CCl}_4)$  7.61 (1 H, sharp s), 7.8br (1 H), and 8.32 (16 H).

**Bicyclo[3.3.2]decane-1,5-diol (1d).**—Chromium trioxide (2.0 g) was added in portions over 90 min to a stirred solution of the hydrocarbon (1a) (1 g) dissolved in acetic acid (15 ml) and acetic anhydride (15 ml), with the reaction temperature maintained below 40 °C. After a further 5 h the mixture was poured onto ice and extracted into methylene chloride, and the combined organic extracts were then washed with 2N-sodium hydroxide (150 ml), and water, dried, and evaporated. The residual yellow oil was dissolved in ether and treated with lithium aluminium hydride as in the preparation of (1b) to give a thick syrup, which crystallised from light petroleum–ether (7 : 3) as white needles (420 mg, 34%), m.p. 214–218° (lit.,<sup>34</sup> 214–217°),  $\nu_{\max}$ . (KBr) 3 280, 2 979, 2 942, 2 920, 2 860, 1 484, 1 464, 1 452, 1 386, 1 232, 1 018, and 1 000  $\text{cm}^{-1}$ ,  $\nu_{\max}$ . ( $\text{CHCl}_3$ ) 3 685, 3 607, 3 450, 2 982sh, 2 871, 1 445, 1 355, 1 330, 1 235, 1 060, 1 060, 1 018, and 1 100  $\text{cm}^{-1}$ ,  $\tau(\text{CDCl}_3)$  8.16 and 8.21 (16 H) and 8.40 (2 H).

**1-Chlorobicyclo[3.3.2]decane (1c).**—Bicyclo[3.3.2]decan-1-ol (90 mg) was added to redistilled thionyl chloride (1 ml). The mixture was set aside for 12 h, then treated with crushed ice and extracted with ether; the combined extracts were washed once with water and dried ( $\text{K}_2\text{CO}_3$ ). Distillation, and sublimation of the residual oil, gave the chloride (45 mg, 44%), m.p. 85–87° (lit.,<sup>34</sup> 85–87°),  $\nu_{\max}$ . 2 983, 2 920, 2 865, 1 484, 1 462, 1 451, 1 358, 1 067, 942, 913, 881, 858, 691, and 624  $\text{cm}^{-1}$ ,  $\tau(\text{CCl}_4)$  7.70 (6 H, m) and 8.34 (11 H, m).

**1,5-Dichlorobicyclo[3.3.2]decane (1e).**—Redistilled thionyl chloride (5 ml) was added to a stirred solution of the diol (1d) (210 mg) in methylene chloride (80 ml). The mixture was stirred at room temperature for 20 h, then poured onto crushed ice, and the organic layer was separated and dried ( $\text{K}_2\text{CO}_3$ ). Distillation followed by vacuum sublimation gave the dichloride, which was recrystallised from methanol to give white needles (154 mg, 64%), m.p. 84–86° (Found: C, 57.7; H, 7.9; Cl, 33.15.  $\text{C}_{10}\text{H}_{16}\text{Cl}_2$  requires C, 57.75; H, 7.8; Cl, 34.2%),  $\nu_{\max}$ . 2 982sh, 2 950, 2 888, 1 485, 1 463, 1 452, 1 365, 922, and 864  $\text{cm}^{-1}$ ,  $\tau(\text{C}_6\text{H}_6)$  7.91, 7.98, and 8.08 (10 H, m) and 8.78 (4 H, m),  $M^+$  – Cl (base peak) 171.094 1 ( $\text{C}_{10}\text{H}_{16}\text{Cl}^+$  requires 171.094 1).

**Bicyclo[3.3.2]dec-9-ene (9a).**—Ethyl chloroformate (0.9 ml) was added over 2 min to a stirred solution of bicyclo[3.3.2]decan-9-ol (900 mg) in pyridine (8 ml) chilled in an ice-bath. The mixture was set aside at 0 °C for 24 h and then poured onto ice-cold hydrochloric acid (2N) and thoroughly extracted with ether. The combined extracts were washed twice with aqueous copper sulphate, dried, and evaporated to give the crude carbonate, which was then heated at 300 °C for 45 min. This crude product was adsorbed on alumina from pentene; elution with the same solvent gave a white solid which was sublimed *in vacuo* and then recrystallised from methanol to give bicyclo[3.3.2]dec-9-ene (380 mg, 48%), m.p. 126–128° (lit.,<sup>34</sup> 128.4–130°), homogeneous to g.l.c. (50 m TCEP capillary column; 100 °C),  $\nu_{\max}$ . 3 022, 2 920, 2 862, 1 655, 1 485vw, sh, 1 459, 1 447, 1 117, 1 092, 870, and 690  $\text{cm}^{-1}$ ,  $\nu_{\max}$ . (KBr) shoulder at 1 485 absent,  $\tau(\text{CCl}_4)$  4.13 (2 H, q), 7.55br (2 H), and 8.45 (12 H).

**Bicyclo[3.3.2]decane-9,10-dione (16).**—A solution of bicyclo[3.3.2]decan-9-one (1.0 g), selenium dioxide (1.4 g), and water (1 ml) in dioxan (80 ml) was heated under reflux for 1 h. Precipitated selenium was filtered from the cooled mixture and the solvent was removed to leave a gum which was washed with pentane. The residue was taken up in chloroform and the solution was filtered through Celite, washed with saturated aqueous sodium thiosulphate, and dried. Removal of the solvent left a bright yellow solid which was sublimed *in vacuo* to give the dione (80 mg, 73%), m.p. 192–193° (Found: C, 71.95; H, 8.35.  $\text{C}_{10}\text{H}_{14}\text{O}_2$  requires C, 72.25; H, 8.5%),  $\nu_{\max}$ . 3 410, 2 938, 2 962, 1 712, 1 485, 1 471, 1 453, 1 365, 1 354, 1 315, 1 288, 1 202, 1 096, 1 080, 1 060, 919, and 896  $\text{cm}^{-1}$ ,  $\lambda_{\max}$ . 421 nm ( $\epsilon$  34),  $\tau(\text{CCl}_4)$  6.96br (2 H), and 8.14 (12 H).

**7,8,9,10-Tetrahydro-6,10-propano-6H-cyclohepta[b]quinoxaline (17).**—A solution of bicyclo[3.3.2]decane-9,10-dione (320 mg) and resublimed *o*-phenylenediamine (196 mg) in ethanol (10 ml) was heated under reflux for 1 h, then evaporated to give a solid which was recrystallised twice from petroleum (100–120 °C) furnishing the quinoxaline (200 mg, 60%), m.p. 124–124.5° (Found: C, 80.6; H, 7.6; N, 11.7.  $\text{C}_{16}\text{H}_{18}\text{N}_2$  requires C, 80.6; H, 7.6; N, 11.75%),  $\nu_{\max}$ . 3 070, 2 865, 1 957, 1 930, 1 906, 1 850, 1 824, 1 488, 1 471, 1 450, 1 440, 1 399, 1 379, 1 327, 1 103, 1 090, 940, 932, 870, 671, 610, and 578  $\text{cm}^{-1}$ ,  $\tau(\text{CCl}_4)$  2.00 (4 H decet), 6.34 (2 H), 8.05, 8.12, and 8.20 (11 H), and 8.4–8.6 (1 H).

**3-Deuteriobicyclo[3.3.2]decan-3-ols (2c and d).**—A solution of bicyclo[3.3.2]decan-3-one (100 mg) in anhydrous ether (10 ml) was added to a stirred slurry of lithium aluminium deuteride (45 mg) in ether (10 ml), and the mixture was heated under reflux for 3 h. Excess of deuteride was then destroyed by careful addition of water to the cooled mixture, which was then filtered, dried, and then evaporated to give the deuterio-alcohols (87 mg, 88%) in an *exo-endo* ratio of 2 : 3 as determined by g.l.c.,  $\nu_{\max}$ . 3 618, 2 920, 2 868, 2 150, 1 464, 1 450, 1 380, 1 073, and 1 047  $\text{cm}^{-1}$ , showing no H-3 resonance.

**3,3-Dideuteriobicyclo[3.3.2]decane (2e).**—3-Deuteriobicyclo[3.3.2]decan-3-ol (80 mg) dissolved in pyridine (0.5 ml) was treated with recrystallised tosyl chloride (110 mg). Normal isolation procedures gave the mixed 3-deuteriobicyclo[3.3.2]decan-3-yl tosylates (120 mg, 79%) as a white crystalline solid,  $\nu_{\max}$ . 3 078, 3 042, 2 930, 2 877, 2 205, 1 919, 1 600, 1 498, 1 469, 1 452, 1 370, 1 259, 1 190, 1 102, 1 020, 960, 915, 871, and 669  $\text{cm}^{-1}$ . A solution of the tosylates in anhydrous ether (10 ml) was added to a stirred slurry of lithium aluminium deuteride (50 mg) in ether (10 ml) and the mixture was heated under reflux for 24 h. Excess of deuteride was destroyed by careful addition of water, and the ethereal solution was filtered from inorganic salts, which were washed with a further portion of ether. The combined organic extracts were analysed by g.l.c. (OV1; 80 °C) which revealed two components in the ratio 3 : 2. Comparison with authentic (undeuteriated) samples identified the minor component as the 3,3-dideuterio-hydrocarbon (2e) and the major component as 3-deuteriobicyclo[3.3.2]dec-2-ene. The mixture was readily separated by preparative t.l.c. on silver nitrate–silica gel (1 : 3), developed with pentane. The faster moving component proved to be the 3,3-dideuterio-hydrocarbon (2e) (24 mg, 20%),  $\nu_{\max}$ . 2 900, 2 870, 2 850, 2 150, 1 458, and 1 442  $\text{cm}^{-1}$ , *m/e* 140/139/138 ( $^2\text{H}_2$  93 1%;  $^2\text{H}_1$  5 2%;  $^1\text{H}_0$  1 7%; number of deuterium atoms per molecule 1.914).



*2,2-Dideuteriobicyclo[3.3.2]decane* (22c).—This compound was prepared by a procedure corresponding to that for the 3,3-isomer. Thus, bicyclo[3.3.2]decan-2-one (100 mg) was reduced in ethereal solution with lithium aluminium deuteride (45 mg). The resultant 2-ols were treated with tosyl chloride (110 mg) in the usual manner to furnish the mixed 2-deuterio-2-yl tosylates, which in turn were treated with lithium aluminium deuteride (50 mg) in ether solution. G.l.c. analysis again showed two components in the ratio 3 : 2. Preparative t.l.c. on silver nitrate-silica gel (1 : 3) (pentane as developing solvent) gave the minor, less polar component, 2,2-dideuteriobicyclo[3.3.2]decane (22c) (30 mg, 25%),  $\nu_{\max}$  2 900, 2 850, 2 150, 1 485sh, 1 465, and 1 455  $\text{cm}^{-1}$ ,  $m/e$  140/139/138 ( $^2\text{H}_2$  94.9%;  $^2\text{H}_1$  4.4%;  $^2\text{H}_0$  0.6%; number of deuterium atoms per molecule 1.942).

*9,10-Bis(trimethylsilyloxy)bicyclo[3.3.2]dec-9-ene* (9b).—Sodium (720 mg) was melted under hot xylene (75 ml) and dispersed by rapid stirring under nitrogen. Trimethylsilyl chloride (6.78 g) was added, followed by diethyl cyclooctane-1,5-dicarboxylate (1 g), and the mixture was stirred vigorously and heated under reflux for 1 h. The cooled mixture was then filtered and distilled to leave a brown residue, a portion of which was distilled (short path) to give the bistrimethylsilyl ether as a viscous oil, b.p. 110–112° at 0.1 mmHg,  $\nu_{\max}$  2 990, 2 960, 2 925, 2 885, 2 860, 1 489, 1 453, 1 301, 1 250, 1 052, and 910  $\text{cm}^{-1}$ ,  $\tau(\text{CCl}_4)$  8.24 (14 H) and 9.9 (6 H) ( $\text{C}_6\text{H}_8$  standard).

*Bicyclo[3.3.2]deca-2,6-diene* (23).—Redistilled thionyl chloride (0.66 ml) was added to a stirred solution of bicyclo[3.3.2]dec-6(7)-en-2-*exo*-ol (400 mg) in dry pyridine (16 ml), and the mixture was then heated at 40 °C for 18 h, poured into ice-water and extracted with isopentane (3 × 15 ml). The combined extracts were washed thoroughly with ice-

cold 2N-hydrochloric acid, dried, concentrated, and analysed by g.l.c. (2% Carbowax 20 M; 80 °C), which showed six major products. The least polar component was isolated by preparative g.l.c. (10% Carbowax 20M; 140 °C) as a white crystalline solid, m.p. 77°, with a characteristic odour and identified as the 2,6-diene (23) on the basis of the following spectral data:  $^{20a} M^+$  134,  $\nu_{\max}$  3 060, 3 014, 2 955, 2 933, 2 898, 2 832, 1 654, 1 462, 1 442, 1 429, 1 396, 1 339, 1 238, 1 064, 1 051, 942, 889, 857, 691, and 634  $\text{cm}^{-1}$ ,  $\tau$  (100 MHz;  $\text{CCl}_4$ ) 4.44 (4 H,  $W_{\frac{1}{2}}$  30 Hz) and 7.50, 7.74, 7.97, and 8.18 (multiplets),  $\tau$  (220 MHz;  $\text{CCl}_4$ ) 4.46 (4 H, two t) and 7.4–8.3 (10 H). This material was identical with an authentic sample of (23) prepared by reduction of bicyclo[3.3.2]deca-2,6,9-triene  $^{20b}$  with di-imide.

*Reduction of Bicyclo[3.3.2]decan-3-one*.—Sodium (30 mg) was added in slivers to a stirred solution of the 3-one (45 mg), in water (0.025 ml) and ether (5 ml) at 0 °C. When all the sodium had been consumed, fresh pieces (30 mg) were added, followed by water (0.025 ml). This process was repeated until no ketone remained. The mixture was then quenched with water, the ethereal layer separated, and the aqueous layer thoroughly extracted with fresh ether. The combined extracts were then washed with water, dried, and evaporated to leave a mixture of *exo*- and *endo*-3-ols as a white solid (40 mg). Acetylation of this mixture in the usual manner followed by g.l.c. analysis (50 m TCEP capillary, 0.1 in diam.; 125 °C) indicated an *exo-endo* 3-acetate ratio of 48 : 52.

We are indebted to the S.R.C. for postgraduate studentships (to M. D. and R. H.) and for funding for the services of the Physico-Chemical Measurements Unit (Harwell).

[5/2402 Received, 11th December, 1975]