

## Transannular Hydride Shifts; the Solvolytic Behaviour of Bicyclo[3.3.2]decan-3-*exo*-yl Toluene-*p*-sulphonate

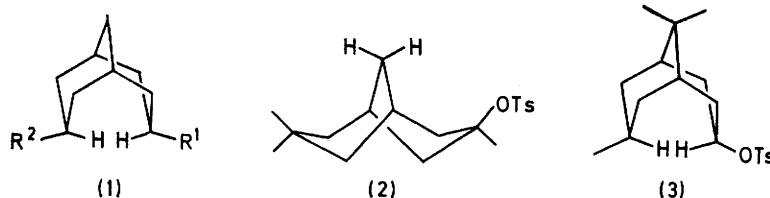
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Bicyclo[3.3.2]decan-3-*exo*-yl tosylate is extremely reactive in buffered acetolysis [ $k_{rel}$  (w.r.t. cyclohexyl)  $9.0 \times 10^3$ ], and gives bicyclo[3.3.2]dec-2-ene (94%) and the corresponding 3-acetates (6%) in the ratio *exo:endo* 5:1. Solvolysis of 2.2.3.4,4-pentadeuteriobicyclo[3.3.2]decan-3-*exo*-yl tosylate is accompanied by a C-7  $\rightarrow$  C-3 transannular hydride shift (48%). The latter result is to be contrasted with the much lesser extent of hydride shift in similar solvolysis of bicyclo[3.3.1]nonan-3-*exo*-yl tosylate.

THE preferred ground state of bicyclo[3.3.1]nonane (1) is a twin-chair<sup>1</sup> conformation, and C-7  $\rightarrow$  C-3 transannular hydride shifts<sup>2</sup> are regularly encountered in equilibrating cationic reactions<sup>3</sup> involving this system. It was therefore surprising to find that buffered acetolysis of a suitably labelled bicyclo[3.3.1]nonan-3-*exo*-yl tosylate (1;  $R^1 = OTs$ ,  $R^2 = H$ ) is accompanied by only ‡ 3.5% hydride shift,<sup>5</sup> at least as far as the major product, the 2-ene (95%), is concerned.‡ Similarly the *exo*-7-methyl-*exo*-tosylate (1;  $R^1 = OTs$ ,  $R^2 = CH_3$ ) is rearranged to a mixture of 3-methylbicyclo[3.3.1]non-2-ene and *exo*-7-methylbicyclo[3.3.1]non-2-ene in the ratio 55:45.<sup>6</sup>

Initially there appeared to be three possible explanations for these low figures. (a) 3-Tosylate groups in

could simply reflect a 'solvolysis' which had in fact proceeded *via* a thermal *cis*-elimination. Recent work<sup>7</sup> from these laboratories has eliminated this possibility. (b) Shiner<sup>8</sup> has demonstrated a conformational dependence of - $\beta$ -deuterium isotope effects upon the solvolysis of *equatorial* cyclohexyl bromomethanesulphonates that is best explained in terms of a transition state of *twist-boat* conformation. This interpretation has found support in the work of Saunders,<sup>9</sup> Whiting,<sup>10</sup> and Sicher,<sup>11</sup> and there is therefore a possibility that (1;  $R^1 = OTs$ ,  $R^2 = H$ ) might react *via* a twist-boat transition state. The bicyclo[3.3.1]nonane skeleton cannot accommodate a twist-boat conformation for the cyclohexanol moiety while the other ring is in a chair arrangement, *i.e.* a *twin twist-boat* (2) is sterically more acceptable and in



this ring system are extremely reactive and unstable above 30 °C, hence the small amount of hydride shift

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‡ Such figures are to be compared with 50% and >95% hydride shift reported<sup>4</sup> for cyclo-octyl and *cis*-5-substituted cyclo-octyl arenosulphonates.

<sup>1</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; 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.

<sup>2</sup> J. Sicher, *Progr. Stereochem.*, 1962, **3**, 202; V. Prelog and J. G. Traynham in 'Molecular Rearrangements,' Part 1, ed. P. de Mayo, Interscience, New York, 1963, pp. 593 *et seq.*; A. C. Cope, M. M. Martin, and M. A. McKervery, *Quart. Rev.*, 1966, **20**, 119.

<sup>3</sup> R. A. Appleton and S. H. Graham, *Chem. Comm.*, 1965, 297; W. A. Ayers and K. Piers, *ibid.*, p. 541; H. Dugas, R. A. Ellison, Z. Valenta, K. Wiesner, and C. M. Wong, *Tetrahedron Letters*, 1965, **18**, 1279; R. A. Appleton, J. R. Dixon, S. C. Egan, and S. H. Graham, *Tetrahedron*, 1967, **23**, 805; E. N. Marvell, J. Seubert, D. Strumer, and W. Federici, *J. Org. Chem.*, 1970, **35**, 396.

this case a direct C-7  $\rightarrow$  C-3 hydride shift is impossible. Ourisson and his co-workers<sup>12</sup> have reported that the 9,9-dimethyl homologue (3) is more reactive than (1;  $R^1 = OTs$ ,  $R^2 = CH_3$ ) in ethanolysis, which is accompanied by virtually 100% hydride shift. While this

<sup>4</sup> (a) A. C. Cope and D. M. Gale, *J. Amer. Chem. Soc.*, 1963, **85**, 3747; (b) A. A. Roberts and C. B. Anderson, *Tetrahedron Letters*, 1969, 3883; (c) W. Parker and C. I. F. Watt, *J.C.S. Perkin II*, in the press; (d) A. C. Cope and D. M. Gale, *J. Amer. Chem. Soc.*, 1963, **85**, 3743; (e) A. C. Cope and R. B. Kinnel, *ibid.*, 1966, **88**, 752; (f) N. L. Allinger and W. Szkrybalo, *Tetrahedron*, 1968, **24**, 4699.

<sup>5</sup> M. A. Eakin, J. Martin, and W. Parker, *Chem. Comm.*, 1968, 298.

<sup>6</sup> M. A. Eakin, J. Martin, W. Parker, S. C. Egan, and S. H. Graham, *Chem. Comm.*, 1968, 337.

<sup>7</sup> M. A. Eakin, J. Martin, W. Parker, and C. I. F. Watt, *J.C.S. Perkin II*, in the press.

<sup>8</sup> V. J. Shiner, jun., and J. G. Jewett, *J. Amer. Chem. Soc.*, 1964, **86**, 945; 1965, **87**, 1382.

<sup>9</sup> W. H. Saunders, jun., and K. T. Finley, *J. Amer. Chem. Soc.*, 1965, **87**, 1384.

<sup>10</sup> N. C. G. Campbell, D. M. Muir, R. R. Hill, J. H. Parish, R. M. Southam, and M. C. Whiting, *J. Chem. Soc.*, 1968, 355.

<sup>11</sup> M. Rankova, J. Sicher, M. Tichy, and M. C. Whiting, *J. Chem. Soc.*, 1968, 365; M. Tichy, J. Hapala, and J. Sicher, *Tetrahedron Letters*, 1969, **43**, 3739.

<sup>12</sup> L. Stéhelin, L. Kanellias, and G. Ourisson, *J. Org. Chem.*, 1973, **38**, 851.

does not constitute proof that (1;  $R^1 = \text{OTs}$ ,  $R^2 = \text{H}$ ) undergoes solvolysis *via* a twin twist-boat transition state \* it does at least demonstrate a powerful conformational influence over the extent of hydride shift in this system. (c) Perhaps owing to the constraint imposed by the C-9 bridge, close approach of C-7 to C-3 in the developing bicyclo[3.3.1]nonan-3-yl cation cannot be realised without concurrent prohibitive strain. Thus the preference of the ion to react by a normal or by a transannular pathway would be determined by the distance between the potential migrating hydrogen atom and the developing carbocationic centre, a separation which would be largely a function of the strain in the system. To test this third possibility we examined the solvolysis of bicyclo[3.3.2]decan-3-*exo*-yl tosylate, in which it appears from Dreiding models that the ethano-bridge, while restricting the number of possible conformations,<sup>13</sup> still permits close approach of C-7 and C-3 without imposing the same degree of steric strain found in bicyclo[3.3.1]nonane.

**Synthesis of Substrates.**—The synthesis of the bicyclo[3.3.2]decane skeleton has received little attention,<sup>14</sup> but in 1957 Alder<sup>15</sup> described the preparation of a mixture of the *exo*- and *endo*-3-ols, (8;  $R = \text{OH}$ ) and (12;  $R = \text{OH}$ ), by deamination of *endo*-6-methylamino-bicyclo[3.2.2]nonane with nitrous acid. We repeated this reaction sequence<sup>16</sup> only to discover that the product is a ten-component mixture † of alcohols, with (8;  $R = \text{OH}$ ) and (12;  $R = \text{OH}$ ) in preponderance. Since none of these alcohols or acetates is readily separable, this route was not considered further.

Instead, bicyclo[3.3.1]non-2-en-9-one<sup>18</sup> ‡ (4) was converted into a mixture of bicyclo[3.3.2]dec-2-en-9-one (5) and -10-one (6) by a variety of ring-expansion procedures, the most acceptable of which involved treatment with ethyl diazoacetate<sup>20</sup> and triethyl-oxonium tetrafluoroborate followed by basic hydrolysis and decarboxylation of the intermediate  $\beta$ -oxo-esters. Subsequent Wolff-Kishner reduction gave the 2-ene (7) as an extremely volatile crystalline solid.

Models of possible transition states for the hydroboration<sup>21</sup> of (7) suggested that attack of diborane on the double bond should occur selectively from the face *exo* to the C-9, C-10 bridge and hence lead to a mixture of the *exo*-3- (8;  $R = \text{OH}$ ) and *exo*-2-ol (9;  $R = \text{OH}$ ). In the event, hydroboration of (7) gave a 65 : 35 mixture of two alcohols, which were then separated by chromatography. Jones oxidation of the more polar alcohol (8;  $R = \text{OH}$ ) gave a ketone (10;  $R = \text{H}$ ) whose n.m.r.

\* Our deuterium kinetic isotope studies directed at this problem will be reported<sup>7</sup> shortly.

† A not unexpected result in the light of Berson's studies<sup>17</sup> on the deamination of *exo*- and *endo*-2-norbornylmethylamines.

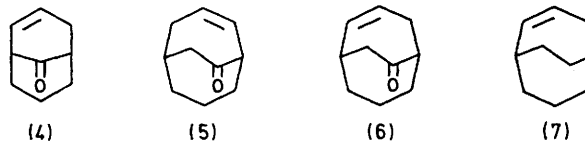
‡ We thank Imperial Chemical Industries, Heavy Organic Division, Billingham, for a sample of this ketone.

<sup>13</sup> See M. Doyle, R. Hafter, and W. Parker, *J.C.S. Perkin I*, 1977, 364, for a conformational analysis of the bicyclo[3.3.2]-decane system.

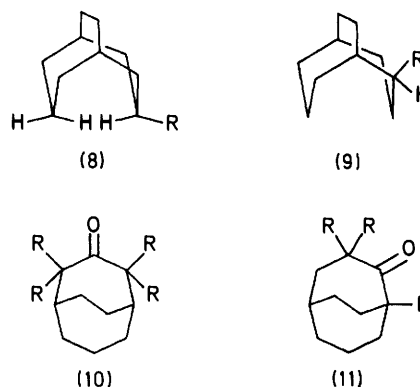
<sup>14</sup> R. S. Henry, W. T. Moodie, W. Parker, and C. I. F. Watt, *J.C.S. Perkin I*, 1975, 803, and references cited therein.

<sup>15</sup> K. Alder, S. Hartung, and G. Hausmann, *Chem. Ber.*, 1956, 89, 1972.

spectrum showed a four-proton singlet at  $\tau$  7.5. In addition, treatment of (10) with sodium-deuterium oxide-dioxan<sup>22</sup> at 95 °C furnished a tetradeuterio-ketone (10;  $R = \text{D}$ ) which showed no n.m.r. signal at



$\tau$  7.5. Similar oxidation of the less polar alcohol (9;  $R = \text{OH}$ ) gave the ketone (11;  $R = \text{H}$ ),  $\tau$  7.2–7.6 (multiplet, 3 H) which on base-catalysed deuteration was converted into a trideuterio-derivative (11;  $R = \text{D}$ ) with no signal at  $\tau$  7.2–7.6. These results show that the more polar alcohol is a bicyclo[3.3.2]decan-3-ol and the less polar 2-ol.



Assignment of the *exo*-configurations [(8) and (9)] to both these alcohols follows from their mode of synthesis and n.m.r. spectra, which in the case of the 3-ol (8;  $R = \text{OH}$ ) shows the C-3 proton signal as a nine-line multiplet ( $J_{\text{AX}} 11$ ,  $J_{\text{BX}} 5$  Hz) centred at  $\tau$  5.7. Such deshielding due to intramolecular interaction with other proximate hydrogen atoms has been widely reported and studied.<sup>23</sup> In a twin-chair conformation of the bicyclo[3.3.2]decane skeleton, the *endo*-protons on C-3 and -7 are very close. It follows that the 2-ol with its more normal  $\text{CH}\cdot\text{OH}$  resonance at  $\tau$  6.1 and associated small couplings (ill-resolved multiplet,  $W_{\frac{1}{2}} 9$  Hz) must also be *exo* in configuration.

Reduction of compounds (10;  $R = \text{H}$ ) and (11;  $R = \text{H}$ ) with lithium aluminium hydride proceeds in a

<sup>16</sup> M. Doyle and W. Parker, *Tetrahedron Letters*, 1970, 945.

<sup>17</sup> J. A. Berson and D. Willner, *J. Amer. Chem. Soc.*, 1964, 86, 609; J. A. Berson and P. Reynolds-Warnhoff, *ibid.*, p. 595.

<sup>18</sup> C. S. Foote and R. B. Woodward, *Tetrahedron*, 1964, 20, 687; S. Brewis and P. R. Hughes, *Chem. Comm.*, 1966, 6.

<sup>19</sup> M. Doyle and W. Parker, *Tetrahedron Letters*, 1970, 3619.

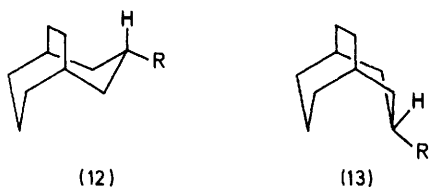
<sup>20</sup> W. L. Mock and M. E. Hartmann, *J. Amer. Chem. Soc.*, 1970, 92, 5767.

<sup>21</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.

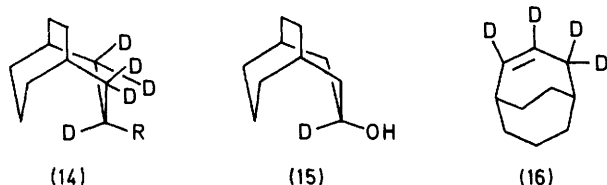
<sup>22</sup> A. F. Thomas, 'Deuterium Labelling in Organic Chemistry,' Appleton-Century-Crofts, Educational Division Meredith Corporation, New York, 1971.

<sup>23</sup> See ref. 13 for a full discussion of this point.

non-stereoselective manner to give *endo-exo* mixtures of the 3-ols (8; R = OH) and (12; R = OH) and 2-ols (9; R = OH) and (12; R = OH) in the ratios 3 : 2 and 1 : 1.6, respectively. This is to be contrasted with the high stereoselectivity encountered in the comparable reductions of bicyclo[3.3.1]nonan-3-<sup>24</sup> and -2-ones<sup>25</sup> where the epimeric mixtures contain 90% *endo*-3-ol and 97% *endo*-2-ol, respectively. Models suggest that the free energy difference between (8; R = OH) and (12; R = OH) is very small, and dissolving metal reduction of the 3-one<sup>13</sup> (10; R = H) gives a mixture of *exo*- and *endo*-3-ols in the ratio 48 : 52. Again this is to be contrasted with bicyclo[3.3.1]nonan-3-one, where under similar conditions the *exo*-3-ol is produced in greater than 90% stereopurity, in fair agreement with the measured<sup>26</sup> free energy difference of  $-2.5$  kcal mol<sup>-1</sup> between the *exo*- and *endo*-3-ols.



To detect the occurrence of transannular hydride migrations in the products from solvolysis of (8; R = OTs), we selected a labelling scheme analogous to that employed by Cope and his co-workers<sup>4</sup> in their corresponding study of the cyclo-octyl system, *viz.* the use of the pentadeuterio-substrate (14; R = OTs). Although the monodeuterio-*exo*-3-ol (15)\* is adequately labelled to detect such shifts, it had to be set aside because of the above lack of stereoselectivity in reduction of the 3-one and severe difficulties encountered in the separation of resultant mixtures.



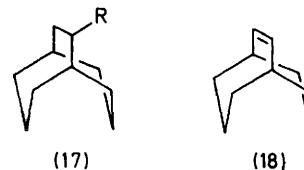
Reduction of (10; R = D) with lithium aluminium deuteride gave a mixture of the *exo*- and *endo*-[<sup>2</sup>H<sub>5</sub>]-3-ols which were converted into the corresponding tosylates and then treated with potassium *t*-butoxide in *t*-butyl alcohol to give a 9 : 1 mixture of 2,3,4,4-tetra-deuteriobicyclo[3.3.2]dec-2-ene and a [<sup>2</sup>H<sub>5</sub>]-butyl ether of undetermined configuration. The olefin (16) was readily purified by chromatography on alumina and subsequent deuterioboration<sup>27</sup>-oxidation, and separ-

\* Reduction of bicyclo[3.3.1]nonan-3-one with sodium-deuterium oxide-ether gives excellent yields of the specifically labelled *endo*-3-deuteriobicyclo[3.3.1]nonan-3-*exo*-ol, which has been used in our more recent work on transannular migrations in this ring system.<sup>7</sup>

<sup>24</sup> M. A. Eakin, Ph.D. Thesis, University of Glasgow, 1967.

<sup>25</sup> J. P. Schaeffer, J. C. Lark, C. A. Flegal, and L. M. Honig, *J. Org. Chem.*, 1967, **32**, 1372.

ation of the *exo*-3- and *endo*-2-ols by preparative t.l.c. gave the desired labelled substrate (14; R = OH). Other bicyclo[3.3.2]decane derivatives required for the identification of solvolysis products, *e.g.* (8; R = OAc), (9; R = OAc), (12; R = OAc), (13; R = OAc), (17; R = OH or OAc), and (18)<sup>13</sup> were prepared by standard procedures.



**Results.**—The relevant kinetic<sup>28</sup> and product distribution data are collected in Tables 1 and 2. The products were identified by co-injection on g.l.c. using

TABLE 1

Rare data for buffered acetolysis of tosylates at 25 °C

	$k_1$	$k_{rel.}$
Bicyclo[3.3.2]decan-3- <i>exo</i> -yl	$4.4 \times 10^{-4}$	9 000
Bicyclo[3.3.1]nonan-3- <i>exo</i> -yl <sup>a</sup>	$5.82 \times 10^{-5}$	1 200
Bicyclo[3.3.1]nonan-3- <i>endo</i> -yl <sup>a</sup>	$7.38 \times 10^{-5}$	
Bicyclo[3.2.1]heptan-3- <i>exo</i> -yl <sup>b</sup>	$4.87 \times 10^{-7}$	10
Bicyclo[3.2.1]heptan-3- <i>endo</i> -yl <sup>b</sup>	$5.32 \times 10^{-6}$	110
Cyclohexyl <sup>c</sup>	$4.88 \times 10^{-8}$	1
Cycloheptyl <sup>c</sup>	$2.57 \times 10^{-7}$	53
Cyclo-octyl <sup>c</sup>	$2.82 \times 10^{-5}$	580
Cyclononyl <sup>c</sup>	$2.43 \times 10^{-5}$	500
Cyclodecyl <sup>c</sup>	$4.69 \times 10^{-5}$	960

<sup>a</sup> Ref. 24. <sup>b</sup> C. W. Jefford, J. Gunsher, and B. Waegell, *Tetrahedron Letters*, 1965, 3405. <sup>c</sup> H. C. Brown and G. Ham, *J. Amer. Chem. Soc.*, 1956, **78**, 2735.

TABLE 2

Analysis of products from buffered acetolysis of bicyclo[3.3.2]decan-3-*exo*-yl tosylate (A) and bicyclo[3.3.1]nonan-3-*exo*-yl tosylate (B)

Tosylate	Products (%) <sup>a</sup>		
	2-ene	<i>exo</i> -3-acetate	<i>endo</i> -3-acetate
(A)	94	5	1
(B) <sup>b</sup>	95	3	2

<sup>a</sup> Stable to reaction conditions. <sup>b</sup> Ref. 24.

capillary columns capable of resolving the *exo*-2, *endo*-2, *exo*-3, *endo*-3, and 9-acetates and the 2- and 9-enes.

The [<sup>2</sup>H<sub>5</sub>]-*exo*-3-tosylate (14; R = OTs) was solvolysed in buffered acetic acid at 25 °C for more than ten half-lives and the product mixture of olefin and acetates was then subjected to hydroboration and the resultant mixture of *exo*-2- and -3-ols separated by preparative t.l.c. Oxidation of the deuteriated 3-ols then gave a mixture of deuteriated 3-ones whose mass spectrum showed parent ions of equal intensity at *m/e* 157 and 155. Subsequent treatment with aqueous sodium hydroxide-dioxan under conditions already established for the

<sup>26</sup> E. N. Marvell and R. S. Knutson, *J. Org. Chem.*, 1970, **35**, 388.

<sup>27</sup> J. Mazur, M. Nassim, F. Sondheimer, and J. Wolfe, *J. Org. Chem.*, 1959, **24**, 1034.

<sup>28</sup> The solvolytic rate constants were determined by the procedure described by C. G. Swain and C. R. Morgan, *J. Org. Chem.*, 1964, **27**, 2097.

complete exchange of hydrogen for deuterium in the tetradeuterio-ketone (10; R = D) furnished a sample of the 3-one whose mass spectrum, after adjustment for isotope effects, corresponded to 2.36 atoms of deuterium per molecule, equivalent to 48% transannular hydride migration.

At the outset of these experiments it had been hoped that the precise location of the remaining deuterium atoms would have emerged from a comparison of the mass spectra of (10; R = H), (10; R = D), and the exchanged ketonic product. Unfortunately, an unequivocal answer to this problem is not yet to hand owing to the complexity of the spectra and the lack, as yet, of additional specifically labelled ketones. In other words, the remaining deuterium atoms in the completely exchanged ketone could be at any position except C-2, -3, or -4. However since we are unable to detect \* the 9-ene or the 9- or the epimeric 2-acetates among the solvolysis products, or the 9-one in the ketonic product from hydroboration-oxidation of this mixture, it seems reasonable to equate the result of this labelling experiment with a specific C-7 → C-3 hydride shift rather than several sequential migrations *via* intermediate cations with associated conformational ring inversions, *e.g.* C-3 → C-9 → C-7, or C-3 → C-2 → C-8 → C-7, or C-3 → C-2 → C-6 → C-7.

There is a notably high retention:inversion ratio (5:1) in the 3-acetates produced from (8, R = OTs) which is to be compared with the lack of stereoselectivity in hydride reduction of the 3-one and the corresponding *exo:endo* ratio (3:2) of 3-acetates obtained from buffered acetolysis of (1; R<sup>1</sup> = OTs, R<sup>2</sup> = H). These data in combination with the high reactivity of (8; R = OTs) and the associated increase in transannular hydride migration tempt one to propose a solvolytic mechanism which involves, to some extent, *endo*-C-7 hydrogen participation in the rate-determining ionisation.

One method for estimating the degree, if any, of such participation is to examine the kinetics of solvolysis of suitably deuteriated substrates; *e.g.* we have recently reported a significant kinetic isotope effect in the solvolysis of *trans*-[5-<sup>2</sup>H<sub>1</sub>]cyclo-octyl bromomethanesulphonate.<sup>6c</sup> With this in mind we have developed a synthetic route to 3,7-disubstituted bicyclo[3.3.2]decane<sup>14</sup> which will allow us to prepare stereospecifically *endo*-7-deuteriobicyclo[3.3.2]decan-*exo*-3-yl tosylate. These kinetic studies and additional experiments to determine the relative extents of transannular hydride shift in the 2-ene and the *exo*- and *endo*-3-acetates are in progress.

#### EXPERIMENTAL

M.p.s were determined for samples in sealed capillary tubes heated in an aluminium block. Mass spectra were

\* Detection limit 0.2%. So far, 2-acetates have not been detected in the solvolysis product from either (1; R<sup>1</sup> = OTs, R<sup>2</sup> = H)<sup>24</sup> or (8; R = OTs),<sup>29</sup> whereas both epimeric 3-acetates are produced during the solvolysis of bicyclo[3.3.2]decan-2-*exo*-yl and *exo*- and *endo*-bicyclo[3.3.1]nonan-2-yl tosylates.

<sup>29</sup> M. Doyle, D.Phil. Thesis, New University of Ulster, 1970.

determined by the Physico-Chemical Measurements Unit at Aldermaston (A.E.I. MS9 spectrometer). U.v. absorption spectra were recorded with a Unicam SP 800 spectrophotometer equipped with the requisite accessories for kinetic studies. Routine i.r. spectra were determined for solutions in carbon tetrachloride (unless stated otherwise) with Perkin-Elmer 157G and 457 spectrophotometers. 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 (tetramethylsilane as internal reference). High resolution n.m.r. spectra were recorded by the P.C.M.U. with 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 on a Perkin-Elmer F11 instrument. Preparative g.l.c. was performed on a Varian Aerograph 700 instrument. Alumina for chromatography was Laporte type H, deactivated with 5% (w/w) water, unless stated otherwise. Thin-layer chromatoplates were prepared from Merck Kieselgel G; preparative plates were 1 mm thick; bands were located on the former with cerium(IV) sulphate-sulphuric acid and in the latter with iodine vapour. Light petroleum refers to the fraction of b.p. 40–60 °C. All organic extracts were dried over anhydrous magnesium sulphate. All compounds containing the bicyclo[3.3.2]decane ring system were treated as if they were both volatile and unstable in air. They were therefore always stored in sealed containers, under nitrogen, at –20 °C.

*syn- and anti-9-Hydroxybicyclo[3.3.1]non-2-ene-9-carbonitrile*.—AnalaR potassium cyanide (132 g) was added over 20 min to a stirred solution of bicyclo[3.3.1]non-2-en-9-one (16.5 g) in anhydrous ethanol (500 ml) and acetic acid (166 ml) at 0 °C. After stirring for 30 min at 0 °C and 2 h at 20 °C, the mixture was poured into an excess of ice-water and extracted four times with ether. The combined extracts were then washed with water, saturated sodium hydrogen carbonate solution, and brine and dried. The solvent was removed on a steam-bath *via* a 24 in Vigreux column to yield a white solid (16 g, 85%) which was recrystallised from ether-light petroleum to furnish needles, m.p. 129–130° (t.l.c. showed two components) (Found C, 73.45; H, 8.2; N, 8.55. C<sub>10</sub>H<sub>13</sub>NO requires C, 73.6; H, 8.05; N, 8.6%),  $\nu_{\max}$  (high resolution) 3 590, 3 450, 3 030, 2 283, 1 645, 1 123, 1 045, 1 010, and 704 cm<sup>-1</sup>,  $\tau$  3.90–4.56 (2 H,m), 6.18 (1 H, s, removed by D<sub>2</sub>O), 7.35–7.72 (10 H, complex),  $M^+$  163.

*syn- and anti-9-Cyanobicyclo[3.3.1]non-2-en-9-yl Acetate*.—The epimeric mixture of cyanohydrins (15.9 g) was mixed with AnalaR acetic anhydride (23 g) and dry pyridine (18.4 g), left at room temperature for 5 days, then treated with an equal volume of saturated sodium carbonate solution and stirred for 30 min before addition of an excess of 6N-hydrochloric acid. Normal work-up followed by removal of the solvent *in vacuo* at ice point yielded a white crystalline solid (20.6 g, 95%). Recrystallisation from ether-light petroleum furnished the epimeric *cyanohydrin acetates* as needles, m.p. 97–98°,  $M^+$  205 (Found: C, 70.4; H, 6.95; N, 6.75. C<sub>12</sub>H<sub>15</sub>NO<sub>2</sub> requires C, 70.2; H, 7.35; N, 6.8%) (t.l.c. showed two spots),  $\nu_{\max}$  (Nujol) 3 060, 2 280, 1 745, 1 225, and 708 cm<sup>-1</sup>,  $\tau$  7.85 (3 H, s) and 3.85–4.58 (2 H, m).

*syn- and anti-9-Methylaminobicyclo[3.3.1]non-2-en-9-ol*.

—The epimeric mixture of cyanohydrin acetates (20 g) in ether (50 ml) was added dropwise with stirring to a slurry of lithium aluminium hydride (15 g) in ether (150 ml) at such a rate that gentle refluxing occurred. The mixture was refluxed for a further hour, and then the excess of hydride was destroyed by dropwise addition of saturated sodium sulphate solution. The mixture was filtered free of the granular precipitate and the ether dried. Removal of the solvent *in vacuo* at ice point furnished a white crystalline solid (15.8 g, 95%). T.l.c. showed two spots. Recrystallisation from ether furnished white needles, m.p. 81–82°,  $\nu_{\max}$  (high resolution) 3 582, 3 540, 3 410, 3 020, 1 650, 1 600, 980, and 705  $\text{cm}^{-1}$ ,  $\tau$  7.4 (1 H, s, removed by  $\text{D}_2\text{O}$ ) and 4–4.6 (2 H, m),  $M^+$  167. The material was hygroscopic and did not give satisfactory analytical figures; it was used directly for the next stage.

*Bicyclo[3.3.2]dec-2-en-9- and -10-one* (5) and (6).—(a) AnalaR sodium nitrite (14 g) in water (40 ml) was added dropwise over 15 min to a stirred solution of the above hydroxy-amines (15.8 g) in water (340 ml) containing acetic acid (40 ml) maintained at  $5 \pm 0.5$  °C. The mixture was stirred for 30 min at ambient temperature and finally heated on a steam-bath for 1 h, during which time a yellow oil separated on the surface. Usual work-up and removal of the ether *in vacuo* at ice point yielded an orange viscous oil (12.7 g). G.l.c. analysis (Carbowax 1 540; 50 m; 0.01 m capillary column; 125 °C) showed the two compounds to be present in equal proportions. The oil was adsorbed on alumina (380 g) (Grade III, neutral) from pentane. Elution with pentane furnished a white, volatile crystalline mixture of bicyclo[3.3.2]dec-2-en-9- and -10-ones, (5) and (6) (7 g, 50%). Vacuum sublimation (80 °C; 0.5 mmHg) yielded a crystalline solid, m.p. 94–96° (Found: C, 79.75; H, 9.35.  $\text{C}_{10}\text{H}_{14}\text{O}$  requires C, 79.95; H, 9.4%),  $\nu_{\max}$  3 390, 3 020, 2 935, 1 704, 1 660, 1 457, 1 448, 1 429, 1 410, 1 401, 1 375, 1 361, and 690  $\text{cm}^{-1}$ . These isomeric ketones could be separated by chromatography on alumina; the less polar component (5) exhibited  $\nu_{\max}$  3 030, 1 705, 1 660, 1 440, 990, and 685  $\text{cm}^{-1}$ ;  $\tau$  3.75–4.68 (2 H, m), 6.75br (1 H), 7.37, 7.41, and 7.54 (5 H, m), and 8.28 (6 H, m). The more polar ketone (6) showed  $\nu_{\max}$  3 040, 1 700, 1 660, 1 355, 1 080, 900, and 690  $\text{cm}^{-1}$ ,  $\tau$  4.11–4.19 (2 H, m), 7.2–7.8 (6 H), and 8.21 (6 H).

(b) Bicyclo[3.3.1]non-2-en-9-one (20 g), potassium hydroxide (9 g), and water (30 ml) were dissolved in methanol (200 ml) and cooled in an ice-salt bath. A solution of *N*-nitroso-*N*-methyltoluene-*p*-sulphonamide (60 g) in methanol (450 ml) was added slowly to the stirred mixture, the reaction temperature being maintained below 20 °C. The mixture was stirred overnight, then diluted with water (1.6 l) and extracted with ether (3 × 200 ml). Distillation of the combined extracts left an oily product, a mixture of methyl tosylate, bicyclo[3.3.1]non-2-ene-9-spiro-oxiran, and bicyclo[3.3.2]dec-2-ene-9- and -10-ones. The mixture was dissolved in ethanol (100 ml), a solution of potassium hydroxide (10 g) in water (70 ml) was added, and the mixture was refluxed for 15 h, then diluted with water (1.5 l) and extracted with pentane (3 × 150 ml). The combined organic extracts were washed with water, and dried, and distilled, leaving an oily product. G.l.c. (Carbowax 20M; 50 ft SCOT column; 150 °C) analysis revealed a mixture of bicyclo[3.3.2]dec-2(3)-en-9-one (70%) and another product (25%). This was adsorbed on alumina from light petroleum and eluted with ether-light petroleum (5:95) to give the by-product (4.75 g, 21%) and bicyclo[3.3.2]dec-2(3)-en-9-

one (10.75 g, 49%), m.p. 94–96°. The by-product is probably bicyclo[3.3.1]non-2-ene-9-carbaldehyde, produced by rearrangement of bicyclo[3.3.1]non-2-ene-9-spiro-oxiran.

(c) Bicyclo[3.3.1]non-2-en-9-one (20 g) and triethyloxonium tetrafluoroborate (50 g) were dissolved in anhydrous methylene chloride (450 ml) under dry nitrogen, and the mixture was cooled to 0 °C. Ethyl diazoacetate (30 ml) was then added with stirring over 1 h and after stirring for 3 h at 0 °C and for a further 2 h at room temperature, saturated sodium hydrogen carbonate solution (500 ml) was added. The mixture was stirred for 1 h, and the organic layer was separated, dried, and evaporated. The residue was taken up in methanol, treated with potassium hydroxide (20 g), and stirred and refluxed for 5 h, then diluted with water (1 l) and extracted with pentane (3 × 100 ml). After normal work-up, the residual white solid was sublimed *in vacuo* to give bicyclo[3.3.2]dec-2-en-9- and -10-one (14 g, 65%), m.p. 94–96°; g.l.c. (Carbowax 20M; 50 ft, SCOT; 150 °C) showed two components in equal amounts.

*Bicyclo[3.3.2]decan-9-one*.—The isomeric enones (5) and (6) (4.5 g) were hydrogenated over 5% palladium-charcoal (0.4 g) in AnalaR ethyl acetate (50 ml). The mixture was then filtered and evaporated *in vacuo* at 40 °C to give a crystalline solid with a 'camphor-like' odour (4.0 g, 89%). T.l.c. and g.l.c. analysis (Carbowax 1 540 on 50 m 0.01 in capillary column at 120 °C; 5% QF1 9 ft column at 120 °C) showed homogeneity. Vacuum sublimation (80 °C; 0.5 mmHg) yielded *bicyclo[3.3.2]decan-9-one* as a waxy solid, m.p. 110–115° (Found: C, 78.75; H, 10.6.  $\text{C}_{10}\text{H}_{16}\text{O}$  requires C, 78.9; H, 10.6%),  $\nu_{\max}$  1 695, 1 470, 1 450, 1 405, 1 212, and 1 105  $\text{cm}^{-1}$ ,  $\tau$  (100 MHz) 7.1 (1 H, s), 7.46 (2 H, d), and 7.75 (1 H, complex),  $M^+$  152. The *p*-bromobenzenesulphonylhydrazone crystallised from chloroform as small prisms, m.p. 214–215 (Found: C, 49.75; H, 5.45; N, 7.25.  $\text{C}_{16}\text{H}_{21}\text{BrNO}_2\text{S}$  requires C, 49.85; H, 5.45; N, 7.3%),  $\nu_{\max}$  (Nujol) 3 300, 1 570, 1 165, 835, and 745  $\text{cm}^{-1}$ ,  $\tau$  (100 MHz) 2.03 (2 H, d) and 2.24 (2 H, d) ( $\text{A}_2\text{B}_2$ ), 6.95br (1 H, s), and 7.65 (2 H, s).

10,10-*Diduteriobicyclo[3.3.2]decan-9-one*.—Bicyclo[3.3.2]decan-9-one (0.105 g) in freshly distilled AnalaR dioxan and a solution of clean sodium metal (0.025 g) in deuterium oxide (2.5 ml) were maintained in a sealed ampoule at 95 °C for 14 days. The mixture was poured into pentane (50 ml) and the layers were separated; normal isolation procedures furnished a waxy solid (0.08 g). Vacuum sublimation (80 °C; 0.5 mmHg) gave the deuterio-ketone as a white crystalline solid,  $\nu_{\max}$  (Nujol) 2 240, 2 160, 1 700, 1 480, 1 120, 1 100, 955, and 810  $\text{cm}^{-1}$ ,  $\tau$  7.1 (1 H, s) and 7.75br (1 H, s) (no doublet at 7.46),  $M^+$  154,  $M + 1$  7%,  $M - 1$  7% (*cf.* starting ketone),  $M + 1$  7.2%,  $M - 1$  7.2% (incorporation of only 2 deuterium atoms).

*Bicyclo[3.3.2]dec-2-ene* (7).—A mixture of bicyclo[3.3.2]dec-2-ene-9- and -10-ones, (5) and (6), (2.52 g) was added to a solution of clean sodium (1.16 g) in diethylene glycol (42 ml). Hydrazine hydrate (100%; 5 ml) was then added and the mixture gently refluxed for 1 h. The bath temperature was then raised to 210 °C; the mixture effervesced and a white solid sublimed onto the water condenser. Vigorous refluxing was continued for 8 h, then the mixture was poured into an excess of water and extracted three times with pentane. After normal work-up, removal of the solvent on a steam-bath *via* a 24 in Vigreux column yielded the olefin as a highly volatile crystalline solid (2.08 g, 80%). A sample purified by sublimation

(20 °C; 0.05 mmHg) gave white *needles*, m.p. 114–116° (Found: C, 88.15; H, 11.65.  $C_{10}H_{16}$  requires C, 88.15; H, 11.85%).  $M^+$  136,  $\nu_{\max}$  3 011, 2 915, 1 655, 1 467, 1 452, 1 448, 1 429, 1 071, and 687  $cm^{-1}$ ,  $\tau$  4.33 (2 H, d), 7.43br, 7.69 (sharp) (4 H), and 8.4 (10 H).

*Bicyclo[3.3.2]decan-3-exo-ol* (8; R = OH) and *-2-exo-ol* (9; R = OH).—Freshly distilled boron trifluoride–ether (1.15 ml) in anhydrous ether (12.5 ml) was added dropwise over 0.5 h to an ice-cold stirred solution of the 2-ene (7) (0.15 g) in anhydrous ether (7 ml) and lithium aluminium hydride (0.4 g) under dry nitrogen and then stirred for 1 h at ambient temperature. AnalaR acetone was then added to destroy the excess of hydride, and 3*N*-sodium hydroxide solution (3 ml) was then added, followed by aqueous hydrogen peroxide (30%; 3 ml), the latter dropwise over 15 min. The mixture was then stirred for 0.5 h and then extracted three times with ether. Normal work-up and removal of the solvent at ice point *in vacuo* yielded a clear oil, which crystallised on prolonged scratching. T.l.c. showed one elongated spot. G.l.c. analysis showed two components in the ratio 65 : 35 (Carbowax 1 540 capillary column; 0.01 in diameter; 120 °C). The two alcohols were separated by multiple-elution (five runs; 10% EtOAc–petroleum) preparative t.l.c. The more polar *alcohol* (8; R = OH), m.p. 138–140°, had  $\nu_{\max}$  (CCl<sub>4</sub>) 3 630, 2 955, 2 905, 1 460, 1 452, 1 042, 1 031, 1 013, and 994  $cm^{-1}$ ;  $\tau$  (100 MHz) 5.70 (1 H, asym. 9-line  $A_2B_2X$  m,  $J_{AX}$  11,  $J_{BX}$  5 Hz), and 8.53 (sharp) (1 H, s, removed by D<sub>2</sub>O) (Found: C, 78.0; H, 11.7.  $C_{10}H_{18}O$  requires C, 77.85; H, 11.75%). The less polar *alcohol* (9; R = OH), m.p. 166–170°, had  $\nu_{\max}$  (CCl<sub>4</sub>) 3 625, 2 955, 1 480, 1 464, 1 452, 1 379, 1 097, 1 027, 993, and 934  $cm^{-1}$ ,  $\tau$  (100 MHz) 6.1 (1 H, m,  $W_{\frac{1}{2}}$  9 Hz) and 8.42 (sharp) (1 H, s, removed by D<sub>2</sub>O) (Found: C, 78.0; H, 11.7.  $C_{10}H_{18}O$  requires C, 77.85; H, 11.75%). From ca. 25 mg of each alcohol, the corresponding acetates were prepared. The *exo-3*-acetate was obtained as a clear oil,  $\nu_{\max}$  2 960, 2 900, 1 733, 1 455, 1 366, 1 257, 1 244, and 1 022  $cm^{-1}$ ,  $\tau$  4.55 (1 H, 9-line  $A_2B_2-X$  m,  $J_{AX}$  11,  $J_{BX}$  5 Hz) and 8.04 (sharp) (3 H, s). The *exo-2*-acetate was also a clear oil,  $\nu_{\max}$  2 965, 2 905, 1 734, 1 462, 1 367, 1 249, 1 234, and 1 015  $cm^{-1}$ ,  $\tau$  5.02 (1 H,  $W_{\frac{1}{2}}$  12 Hz) and 8.02 (sharp) (3 H, s).

G.l.c. analysis of these acetates indicated an epimeric purity of 95%. Two recrystallisations from pentane were sufficient to bring each alcohol to 99% epimeric purity. An attempt to increase the ratio of *exo-3*- to *exo-2*-ol by hydroboration with di-isopentylborane was not successful.

*Bicyclo[3.3.2]decan-3-one* (10; R = H).—To the *exo-3*-ol (8; R = OH) (0.04 g) in AnalaR acetone (4 ml) at 0 °C, 8*N*-Jones reagent was added dropwise with stirring until a red colouration persisted. Usual work-up and removal of the solvent at ice point *in vacuo* afforded a white crystalline solid (0.035 g) with a camphoraceous smell. The material was purified by sublimation (0.1 mmHg) at 70 °C;  $M^+$  152 (Found: C, 78.8; H, 10.55.  $C_{10}H_{16}O$  requires C, 78.9; H, 10.6%),  $\nu_{\max}$  2 920, 1 710sh, 1 698, 1 465, 1 415, and 1 185  $cm^{-1}$ .

*2,2,4,4-Tetradeuteriobicyclo[3.3.2]decan-3-one* (10; R = D).—Treatment of the 3-one (10; R = H) (0.05 g) with ca. 0.1*M*-sodium deuterioxide in dioxan (2.5 ml) in the usual manner yielded a tetradeuterio-ketone (0.04 g),  $M^+$  156,  $\nu_{\max}$  2 925, 2 875, 2 200, 2 180, 2 160, 1 695, 1 462, 1 335, 1 167, and 1 135  $cm^{-1}$ ; no n.m.r. singlet at  $\tau$  7.44.

*exo- and endo-Bicyclo[3.3.2]decan-3-ol* (8; R = OH) and (12; R = OH).—Lithium aluminium hydride reduced

the 3-one (10; R = H) (0.08 g) in ether to yield a crystalline solid (0.07 g),  $\nu_{\max}$  3 650, 3 500, 2 950, 1 460, 1 380, 1 060, and 1 020  $cm^{-1}$ ,  $\tau$ (CCl<sub>4</sub>) 5.5–6.5 (complex in 6.1–6.2 (H-3,  $J_{AX+BX}$  ca. 20 Hz), and 7.5 (sharp s).

Acetylation and g.l.c. analysis of the mixture indicated two components (Carbowax 1 540; 135 °C) in the ratio 60 : 40, the latter being identical with the acetate of the more polar alcohol from hydroboration of the 2-ene (7).

*Bicyclo[3.3.2]decan-2-one* (11; R = H).—Jones oxidation of the *exo-2*-ol (9; R = OH) (0.100 g) yielded the 2-one (0.08 g) as a highly crystalline solid. A sample was purified by vacuum sublimation (80 °C; 0.1 mmHg),  $M^+$  152 (Found: C; 79.05; H, 10.6.  $C_{10}H_{16}O$  requires C, 78.9; H, 10.6%),  $\nu_{\max}$  2 930, 1 706, 1 465, and 1 455  $cm^{-1}$ ,  $\tau$  7.2–7.6 (3 H, complex m).

*1,3,3-Trideuteriobicyclo[3.3.2]decan-2-one* (11; R = D).—Treatment of the above 2-one (0.10 g) with ca. 0.1*M*-sodium deuterioxide in dioxan (5 ml) in the usual manner yielded a trideuterio-ketone (0.80 g),  $M^+$  155,  $\nu_{\max}$  2 920, 2 215, 2 160, 2 130, 1 702, 1 450, 1 274, 1 161, and 1 106  $cm^{-1}$ ; no n.m.r. multiplet at  $\tau$  7.2–7.6.

*exo- and endo-Bicyclo[3.3.2]decan-2-ol* (9; R = OH) and (13; R = OH).—Lithium aluminium hydride reduced the 2-one (11; R = H) (0.42 g) in ether to furnish a crystalline solid (0.038 g),  $\nu_{\max}$  3 660, 3 500, 2 950, 1 460, 1 060, 1 020, 1 000, 960, and 940  $cm^{-1}$ . Acetylation and g.l.c. analysis of the mixture (Carbowax 1 540; 135 °C) indicated two components in the ratio 35 : 65, the latter being identical with the acetate of the less polar alcohol from hydroboration of the 2-ene (7).

*Bicyclo[3.3.2]decan-9-ol* (17; R = OH).—A solution of the 9-one (0.065 g) was added dropwise with stirring to a slurry of lithium aluminium hydride (0.06 g) in anhydrous ether (40 ml) at such a rate as to maintain gentle refluxing. The mixture was then refluxed gently for 1 h. Normal work-up and removal of the ether *in vacuo* at ice point yielded a crystalline *solid* (0.055 g, 90%), which was homogeneous to g.l.c. (TCEP 50 m 0.01 in capillary; 135 °C) (Found: C, 77.95; H, 11.8.  $C_{10}H_{18}O$  requires C, 77.9; H, 11.75%),  $\nu_{\max}$  3 670, 3 600, 3 040 2 920, 1 483, 1 450, and 1 020  $cm^{-1}$ ,  $\tau$  5.90 (1 H,  $W_{\frac{1}{2}}$  20 Hz) and 8.55 (1 H, removed by D<sub>2</sub>O).

*Bicyclo[3.3.2]decan-9-yl Acetate*.—The following acetylation procedure was used for the preparation of all acetates. The 9-ol (0.04 g) was treated with AnalaR acetic anhydride (0.65 ml) and anhydrous pyridine (1 ml) and was kept at room temperature for 16 h. The mixture was then poured into dilute sodium hydrogen carbonate solution and extracted three times with pentane. The extracts were washed with 0.5*M*-sulphuric acid, water, and brine and dried. Removal of the pentane at ice-point *in vacuo* yielded a clear oil (0.049 g) with a sweet smell. The material was homogeneous to g.l.c. analysis (TCEP 50 m 0.01 in capillary column; 125 °C);  $\nu_{\max}$  2 940, 2 890, 1 733, 1 486, 1 366, 1 245, 1 015, and 963  $cm^{-1}$ ,  $\tau$  5.1 (1 H, m,  $W_{\frac{1}{2}}$  22 Hz) and 8.13 (3 H, s).

*Bicyclo[3.3.2]decan-3-yl Toluene-p-sulphonate* (8; R = OTs).—Treatment of the *exo-3*-ol (0.077 g) with toluene-*p*-sulphonyl chloride (0.4 ml) in the usual manner yielded a clear oil which crystallised on scratching to give an extremely unstable white solid. Recrystallisation at –70 °C from *n*-pentane furnished the *tosylate*, m.p. 88–89° (Found: C, 66.35; H, 7.7.  $C_{17}H_{24}O_3S$  requires C, 66.2; H, 7.85%),  $\nu_{\max}$  3 020, 2 950, 2 890, 1 387, 1 343, 1 189, 1 178, 913, and 907  $cm^{-1}$ ,  $\tau$  2.0, 2.12, 2.46, and 2.60 (4 H,

$A_2B_2q$ ), 4.8 (1 H, asym. 9-line m, X of  $A_2B_2X$ ,  $J_{AX} 11 J_{BX}$  5 Hz), and 7.5 (sharp) (3 H, s). Owing to its instability this material was always used immediately.

**Buffered Acetolysis of Bicyclo[3.3.2]decan-3-exo-yl Tosylate.**—The tosylate (8; R = OTs) (0.042 g) was solvolysed in anhydrous buffered acetic acid (41 ml) (1.2M in sodium acetate with respect to tosylate) at 25 °C for 24 h. The mixture was then poured into an excess of ice-water and extracted thoroughly with pentane. The combined extracts were washed with water, sodium hydrogen carbonate solution, and brine, and dried. G.l.c. analysis (TCEP 50 m 0.01 in capillary column, 140 °C) showed (by co-injection of authentic samples) the products to be bicyclo[3.3.2]dec-2-ene (7) (94%), the *exo*-3-acetate (8; R = OAc) (5%), and the *endo*-3-acetate (12; R = OAc) (1%).

**Elimination with Potassium Butoxide.**—To potassium metal (0.025 g) in anhydrous *t*-butyl alcohol (10 ml) was added a solution of the tosylates (8; R = OTs) and (12; R = OTs) (0.16 g) in dry *t*-butyl alcohol (5 ml). The mixture was refluxed gently, and after about 30 min a white precipitate had developed. Refluxing was continued for 24 h. Normal work-up and removal of the pentane at ice point *in vacuo* yielded a highly volatile crystalline solid (0.66 g),  $\nu_{\max}$  (Nujol) 3 030, 2 950, 1 460, and 705  $\text{cm}^{-1}$ ,  $\tau$  4.4 (2 H, d). G.l.c. analysis (Carbowax 1 540; 50 m capillary column; 110 °C) showed two components, the 2-ene (7) (92%) and a more polar component (8%).

**2,2,4,4-Tetradeteriobicyclo[3.3.2]decan-3-one** (10; R = D).—The 3-one (10; R = H) (0.95 g) was deuterated in the usual manner with clean sodium (0.27 g), deuterium oxide (26 ml; 99.7%), and AnalaR dioxan (26 ml). Careful work up furnished a crystalline solid (0.94 g),  $\nu_{\max}$  2 925, 2 875, 2 200, 2 180, 2 160, 1 695, 1 462, 1 335, 1 167, and 1 135  $\text{cm}^{-1}$ ,  $M^+$  156 (0.74%  $^2\text{H}_2$ ; 9%  $^2\text{H}_3$ ; 89.8%  $^2\text{H}_4$ ; *i.e.* 3.895  $^2\text{H}$  per molecule).

**Reduction of the Tetradeterio-3-one with Lithium Aluminium Deuteride.**—The tetradeterio-3-one (10; R = D) (0.89 g) was reduced in ether with lithium aluminium deuteride (CIBA; 99 atom %  $^2\text{H}$ ; 0.40 g) in the usual manner, with rigorous exclusion of moisture, yielding a white crystalline solid (0.715 g),  $\nu_{\max}$  3 450, 2 200, 2 120, 1 460, 1 050, and 1 020  $\text{cm}^{-1}$ . G.l.c. analysis (Carbowax 1 540; 50 capillary; 125 °C) indicated two components in the ratio 60 : 40.

**Formation of the Mixed [ $^2\text{H}_5$ ]Tosylates corresponding to (8; R = OTs) and (12; R = OTs).**—Treatment of the above mixed [ $^2\text{H}_5$ ]alcohols (0.715 g) with toluene-*p*-sulphonyl chloride (0.983 g) in anhydrous pyridine (4.5 ml) yielded a highly crystalline solid, (1.49 g),  $\nu_{\max}$  3 030, 2 950, 2 200, 2 100, 1 605, 1 463, 1 760, 1 180, 1 160, 900, and 880  $\text{cm}^{-1}$ , which was immediately used for the next experiment.

**2,3,4,4-Tetradeteriobicyclo[3.3.2]dec-2-ene** (16).—A solution of cleaned potassium metal (0.210 g) in *t*-butyl alcohol (25 ml) was added to the above tosylates (1.49 g) in absolutely dry *t*-butyl alcohol (5 ml). The mixture was refluxed for 2 h, then worked up in the usual manner to yield a waxy crystalline solid (0.568 g),  $\nu_{\max}$  (mull) 2 950, 2 250, 2 175, 2 140, 2 070, and 1 640  $\text{cm}^{-1}$ ,  $M^+$  140. G.l.c. analysis indicated (Carbowax 1 540; 50 m capillary; 50 °C) a small amount of impurity (8%). Separation was effected by chromatography on Grade III alumina. The olefin eluted with *n*-pentane was obtained as a waxy solid (0.48 g). Elution with ether gave a clear oil (20 mg),  $\nu_{\max}$  2 950, 1 460, 1 370, 1 125, and 1 090  $\text{cm}^{-1}$ ,  $M^+$  215.

**Deuterioboration of the [ $^2\text{H}_4$ ]Olefin; Preparation of the**

**Alcohol** (14; R = OH).—Deuterioboration of the olefin (16); (0.48 g) according to the method of Sondheimer<sup>27</sup> with lithium aluminium deuteride (CIBA; >99 atom %  $^2\text{H}$ ) in place of the hydride yielded a white solid (0.53 g),  $\nu_{\max}$  3 450, 2 170, 2 080, 1 450, 1 370, 1 100, 1 080, 1 010, 950, and 940  $\text{cm}^{-1}$ . G.l.c. analysis indicated (Carbowax 1 540; 50 capillary; 125 °C) mainly two components in the ratio 65 : 35, together with a small amount of unchanged olefin. The [ $^2\text{H}_5$ ]-*exo*-3- and -*exo*-2-ols were separated as for the undeuterated alcohols, by multiple elution (five runs) preparative t.l.c. The [ $^2\text{H}_5$ ]-*exo*-3-ol (14; R = OH) (0.197 g) showed  $\nu_{\max}$  3 450, 2 170, 2 080, 1 450, 1 075, and 950  $\text{cm}^{-1}$ ,  $M^+$  159 (low intensity), *m/e* 141 (base peak); and the [ $^2\text{H}_5$ ]-*exo*-2-ol (0.07 g),  $\nu_{\max}$  3 450, 2 170, 2 075, 1 450, 1 100, 1 080, and 940  $\text{cm}^{-1}$ ,  $M^+$  159 and 141 (both medium intensity).

**The Pentadeuterio-tosylate** (14; R = OTs).—The [ $^2\text{H}_5$ ]-*exo*-3-ol (0.197 g) was rapidly tosylated by treatment with toluene-*p*-sulphonyl chloride (275 mg) in dry pyridine (1 ml) yielding a white crystalline solid (0.37 g),  $\nu_{\max}$  3 020, 2 160, 2 130, 1 600, 1 495, 1 180, 1 175, and 900  $\text{cm}^{-1}$ , purified by two crystallisations from *n*-pentane (−70 °C); m.p. 85—87°. This material was at once used for the next stage.

**Buffered Acetolysis of 2,2,3,4,4-Pentadeuteriobicyclo[3.3.2]decan-3-exo-yl Tosylate** (14; R = OTs).—The above tosylate (0.25 g) was added to a solution (15 ml) of anhydrous glacial acetic acid containing fused sodium acetate (0.12 g). The mixture was maintained at 25 °C for 22 h and then poured into ice-water and extracted four times with pentane-ether (1 : 1). Normal work-up and careful removal of the solvent (24 in Vigreux column) yielded a waxy solid (0.156 g),  $\nu_{\max}$  3 030, 2 220, 2 160, 2 110, 2 070, 1 735, 1 650, 764, and 610  $\text{cm}^{-1}$ .

**Hydroboration of the Solvolysis Product.**—The above solvolysis product (0.156 g) was hydroborated by Sondheimer's *in situ* method<sup>27</sup> yielding a white solid (0.16 g),  $\nu_{\max}$  (Nujol) 3 450, 2 150, 2 060, 1 450, 1 015, and 945  $\text{cm}^{-1}$ . The 3-ols were separated from the 2-ols by multiple-elution preparative t.l.c. (five elutions with 10% ethyl acetate-light petroleum), yielding a white solid (0.08 g),  $\nu_{\max}$  (Nujol) 3 400, 2 150, 2 060, 1 460, 1 375, 1 060, 1 020, 1 000, and 950  $\text{cm}^{-1}$ .

**Oxidation of the Partially Deuterated 3-Ols.**—The alcohols (0.08 g) were oxidised with Jones reagent in the usual manner yielding a mixture of 3-ones (0.07 g) as a white crystalline solid,  $\nu_{\max}$  2 950, 2 180, 2 110, 2 080, 1 695, and 1 460  $\text{cm}^{-1}$ ,  $M^+$  157 (intense) *m/e* 155 (equally intense) (40.3%  $^2\text{H}_3$ ; 18.7%  $^2\text{H}_4$ ; 36.3%  $^2\text{H}_5$ ; 4.7%  $^2\text{H}_6$ ; 4.05 deuterium atoms per molecule). G.l.c. analysis showed one component (TCEP 50; 0.01 in capillary column; 125 °C), identical with the 3-one (10; R = H). No 9-one was present.

**Base-catalysed Exchange of Deuterium Atoms  $\alpha$  to the Carbonyl Group.**—The 3-one mixture (0.075 g) was treated with clean sodium *ca.* 18 mg in water (2 ml) and dioxan (2 ml) and maintained in a sealed ampoule at 80 °C for 1 week. Normal isolation yielded a crystalline solid (0.06 g). The material was sublimed *in vacuo* (0.25 mmHg; 100 °C);  $\nu_{\max}$  2 940, 2 160, 2 100, 2 060, 1 695, 1 460, and 1 180  $\text{cm}^{-1}$ ,  $M^+$  157 *m/e* 152 (45.4%  $^2\text{H}_0$ ; 8.21%  $^2\text{H}_1$ ; 0%  $^2\text{H}_2$ ; 0.82%  $^2\text{H}_3$ ; 4.01%  $^2\text{H}_4$ ; 41.35%  $^2\text{H}_5$ ; 0.58%  $^2\text{H}_6$ ; number of deuterium atoms per molecule 2.359).

**Pilot experiment.** The [ $^2\text{H}_4$ ]-3-one (50 mg) was treated with water (1.3 ml), dioxan (1.3 ml), and clean sodium (12

mg). The mixture was maintained at 80 °C in a sealed ampoule for 48 h. Work-up as above yielded the 3-one (40 mg) as a crystalline solid,  $\nu_{\text{max}}$  (CCl<sub>4</sub>) 2 940, 2 880sh, 1 698, 1 462, 1 412, 1 345, and 1 180 cm<sup>-1</sup>. The mass spectrum of this ketone sample showed no peak other than natural abundance above  $m/e$  152. Mass spectrometric measurements of % deuterium incorporation were made at electron beam energies of 70, 50, 20, 10, and 5 eV to ensure that the measured peak intensities were meaningful, *i.e.*

that the deuteriated and unlabelled parent peak ratio in the partially deuteriated mixture did not change with beam energy.<sup>30</sup> These measurements are also corrected for isotope effects.

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<sup>30</sup> For an excellent summary of the assumptions implicit in a mass spectral determination of this type, see K. Biemann, 'Mass Spectrometry—Organic Chemical Applications,' McGraw-Hill, New York, 1962.

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