The Solvolytic Behaviour of *exo*- and *endo*-Bicyclo[3,2,1]octane-6-toluene-*p*-sulphonates

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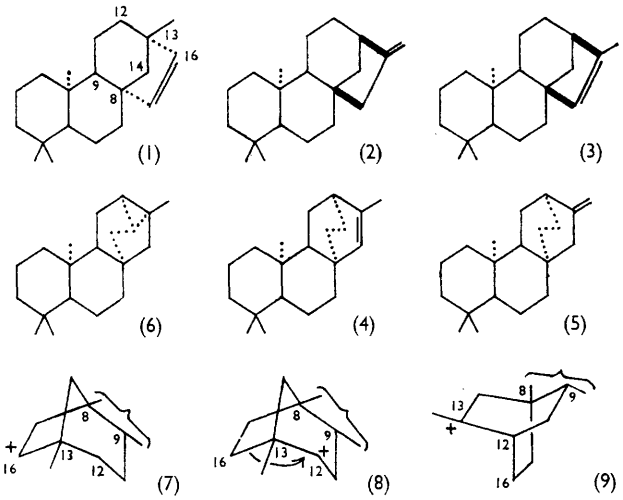
The buffered acetolysis of *exo*-bicyclo[3,2,1]octane-6-toluene-*p*-sulphonate (12; R = OTs) has been found to give *exo*-2-bicyclo[3,2,1]octyl acetate, 40% (16; R = OAc), 2-bicyclo[2,2,2]octyl acetate, 44% (17; R = OAc), and *exo*-6-bicyclo[3,2,1]octyl acetate, 16% (12; R = OAc), whereas the corresponding *endo*-6-isomer (13; R = OTs) gave (16; R = OAc), 19%, (17; R = OAc), 21%, and (12; R = OAc), 60%. The significance of these results and those obtained from similar treatment of tricyclo[3,2,1,$0^{2,7}$]octane is discussed in terms of a hitherto unobserved 4,6-hydride shift in the bicyclo[3,2,1]octane skeleton.

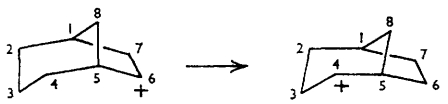
RECENTLY it was found that stachene (1) could be converted into a mixture of kaurene (2), isokaurene (3), isoatisirene (4), and atisirene (5) [1] by treatment with hydrochloric acid in chloroform solution. The pentacyclic diterpene trachylobane (6) was discounted as the sole product-forming intermediate in these rearrangements since the (iso)atisirene : (iso)kaurene product ratio differed substantially dependent on whether it was derived from stachene or trachylobane, and so it was suggested that the stachene ⟶ isoatisirene/atisirene rearrangement could be rationalised by invoking a hydride shift from C-12 to C-16 followed by a Wagner–Meerwein rearrangement of the ethano-bridge to C-12 [*i.e.* part structures (7) ⟶ (8) ⟶ (9)].

Although there is ample evidence [2–12] of such 1,3-hydride shifts occurring in the bicyclo[2,2,1]heptane series, at

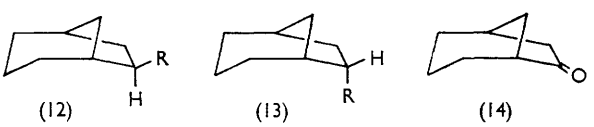
[1] R. A. Appleton, A. J. McAlees, A. McCormick, R. McCrindle, and R. D. H. Murray, *J. Chem. Soc.* (*C*), 1966, 2319.
[2] Review, by J. A. Berson, in 'Molecular Rearrangements, Part One,' ed. P. de Mayo, Interscience, New York, 1963, p. 111.
[3] S. Winstein and D. Trifan, *J. Amer. Chem. Soc.*, 1952, **74**, 1147, 1154.
[4] J. D. Roberts and C. C. Lee, *J. Amer. Chem. Soc.*, 1951, **78**, 5009; J. D. Roberts, C. C. Lee, and W. H. Saunders, *ibid.*, 1954, **76**, 4501.
[5] A. Colter, E. C. Friedrich, J. N. Holness, and S. Winstein, *J. Amer. Chem. Soc.*, 1965, **87**, 378.
[6] J. A. Berson and P. W. Grubb, *J. Amer. Chem. Soc.*, 1965, **87**, 4016.
[7] B. M. Benjamin and C. J. Collins, *J. Amer. Chem. Soc.*, 1966, **88**, 1556.
[8] C. C. Lee and L. K. M. Lam, *J. Amer. Chem. Soc.*, 1966, **88**, 2831.
[9] C. J. Collins, Z. F. Cheena, R. G. Werth, and B. M. Benjamin, *J. Amer. Chem. Soc.*, 1964, **86**, 4913.
[10] M. Saunders, P. von R. Schleyer, and G. A. Olah, *J. Amer. Chem. Soc.*, 1964, **86**, 5680.
[11] C. J. Collins and B. M. Benjamin, *J. Amer. Chem. Soc.*, 1967, **89**, 1652.
[12] J. A. Berson, J. H. Hammons, A. W. McRowe, R. G. Bergman, A. Remanick, and D. Houston, *J. Amer. Chem. Soc.*, 1967, **89**, 2573, 2581, 2590.



the time the present investigation was begun, there was no recorded case of a corresponding 4,6-shift [*i.e.* (10)⟶(11)] in the simple bicyclo[3,2,1]octane system. Accordingly it was decided to examine the solvolytic behaviour of *exo*- and *endo*-6-substituted bicyclo[3,2,1]octanes, (12) and (13), particularly from the standpoint of determining the nature of the *kinetically controlled* products.



3-Bromobicyclo[3,2,1]oct-3-en-6-yl formate [13] was prepared by the addition of dibromocarbene to norbornadiene followed by lithium aluminium hydride reduction and addition of formic acid across the 6,7-double bond. Catalytic hydrogenation in basic solution then gave a mixture of the *exo*- and *endo*-bicyclo[3,2,1]octan-6-ols (in the ratio 25 : 1), which was readily separated by preparative thin-layer chromatography or, more conveniently, by fractional crystallisation from n-pentane. In the ^{1}H n.m.r. spectrum of the more abundant isomer, m.p. 143—144°, the carbinyl proton appeared as a broadened doublet at τ 5·70 (J 7 c./sec.), whereas the corresponding proton in the spectrum of the other alcohol, m.p. 192—194°, appeared at τ 5·50 ($W_{\frac{1}{2}}$ 22 c./sec.). Oxidation of both isomers gave the same ketone [13] (14) which on lithium aluminium hydride reduction was converted predominantly into the alcohol, m.p. 192°.

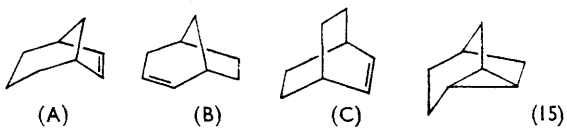


The above spectral and chemical evidence is compatible with stereo-formulae (12; R = OH) and (13; R = OH) for the alcohols m.p. 143° and 192° respectively.

The corresponding toluene-*p*-sulphonates (12 and 13; R = OTs) were then prepared, individually subjected to buffered acetolysis in sealed ampoules at 105° for 100 half-lives, and the nature and distribution of the products determined (see Tables 1 and 2). The relevant bicyclo-

TABLE 1

Olefins * produced from buffered acetolysis of (12 and 13; R = OTs)



	(A)[26]	(B)[28]	(C)[30]	(15)[34]
(12; R = OTs)	100%	—	—	—
(13; R = OTs)	60%	40%	—	—

* Compounds (A), (B), and (C) were stable to the buffered acetolysis conditions.

TABLE 2

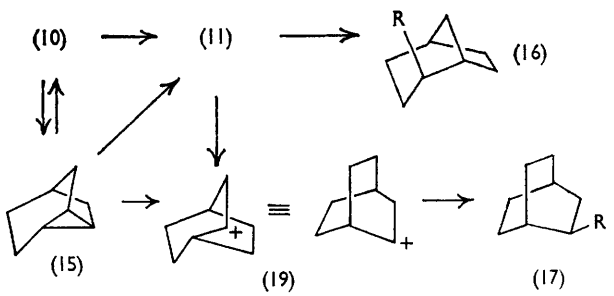
Acetates * formed from buffered acetolysis of (12; R = OTs), (13; R = OTs), and (15)

	(12; R = OAc)	(13; R = OAc)	(16; R = OAc) [29]	(17; R = OAc) [29]	(18; R = OAc) [29]
(12; R = OTs)	16%	0	40%	44%	<1%
(13; R = OTs)	60%	0	19%	21%	0
(15)	26%	0	33%	35%	6%

* All these acetates were stable to the buffered acetolysis conditions.

[3,2,1]-, bicyclo[2,2,2]-, and tricyclo[3,2,1,$0^{2,7}$]-octyl derivatives required for comparison purposes were prepared by well established procedures. The olefinic products were readily analysed by gas–liquid chromatography (g.l.c.) whereas the composition of the acetate fraction was determined by high-resolution n.m.r. spectroscopy at 100 Mc./sec. in the 8 τ region. A complete separation by g.l.c. of all the acetates (or the corresponding alcohols) formed in these solvolyses was not realised; nevertheless, the results of a partial g.l.c. separation reinforced the conclusions as to product distribution based on n.m.r. data.

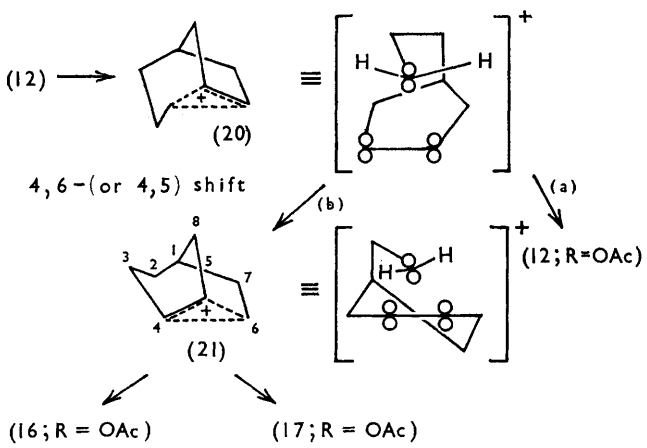
The first important feature which emerges from a consideration of Tables 1 and 2 is the large amount of *exo*-2-bicyclo[3,2,1]- and 2-bicyclo[2,2,2]octyl acetates (16 and 17; R = OAc) produced from the solvolysis of



[13] K. B. Wiberg and B. A. Hess, *J. Org. Chem.*, 1966, **31**, 2250; R. R. Sauers and J. A. Biesler, *Tetrahedron Letters*, 1964, 2181.

(12; R = OTs). Formally this can be explained either by a 4,6-hydride shift in the classical cation (10) leading to (11), and thence by Wagner–Meerwein rearrangement to (19) or by the formation of tricyclo[3,2,1,$0^{2,7}$]octane (15) by proton loss from (10) followed by acid-catalysed cyclopropane ring-opening to (10), (11), and (19). However, the product distribution obtained from buffered acetolysis of (15) illustrates that this hydrocarbon cannot be the sole intermediate by which (16 and 17; R = OAc) are formed, since this would demand the formation of *at least* 6% of *endo*-2-bicyclo[3,2,1]octyl acetate (18; R = OAc). In fact, allowing for a detection limit for (18; R = OAc) of 1%, the mechanism involving tricyclo[3,2,1,$0^{2,7}$]octane as the key intermediate cannot be operative to more than 20%. In addition, the lack of a detectable quantity of (18; R = OAc) in comparison with the large amount of (16 and 17; R = OAc) formed is characteristic of the solvolytic behaviour of (16; R = OTs),[14] (17; R = OTs),[15] and cyclohex-3-enylethyl-*p*-bromo-benzene sulphonate.[16] In other words, the formation of (16 and 17; R = OAc) from (12; R = OTs) would suggest the intermediacy of the non-classical species (21) or a rapidly equilibrating pair of the corresponding classical cations.[17]

When this proposal is taken in conjunction with the formation of unrearranged acetate (12; R = OAc) of retained stereochemistry from (12; R = OTs), itself suggestive of a mesomeric 6-cation (20),* the mechanistic scheme illustrated can be formulated as the major product-forming pathway for the solvolysis of (12; R = OTs).



Ionisation of (12; R = OTs) with participation of the 4,5-sigma-bond will lead to the non-classical ion (20) which can (a) suffer solvent capture either at C-5 or C-6 since these positions are equivalent to give (12; R = OAc), or (b) undergo 4,6-(or 4,5)-hydride shift leading to the bridged species (21) from which (16 and 17; R = OAc) are readily formed. It sould appear from the results in Table 2 that hydride shift (16 and 17; R = OAc) is extremely competitive with counter-ion capture, and this may be due to the greater overall strain and larger number of non-bonded interactions associated with (20) as compared with (21), as becomes apparent from an examination of molecular models.

It can also be seen from a model of (20) [18] that in the most favourable arrangement for overlap of the *p*-orbital at C-4 with the π-orbitals at C-5,C-6, the two C-4 hydrogen atoms are *not* equivalent (cf. the C-6 protons in the 2-bicyclo[2,2,1]heptyl non-classical ion). However, a simple conformational flip of the C-2—C-4 chain produces the enantiomeric structure in which the relative positions of the C-4 protons are reversed. Hence, this proposed conformational equilibrium serves to make *both* C-4 protons favourably situated to adopt the theoretically favourable 'edge-protonated' cyclopropane [3,5,19] (and cf. ref. 4) species, which is consistent with the known *endo,endo* geometry of a 6,2-hydride shift in the related bicyclo[2,2,1]heptyl system.[6,7,12] Hence, the 4,6- and 4,5-hydride shifts become equally probable.

The solvolysis of (13; R = OTs) gives exclusively (16 and 17; R = OAc) in terms of rearranged products, but there is a much higher proportion of 6-acetate (12; R = OAc) notable in the high degree of *exo*-product from *endo*-starting material. In this context, it may be that (13; R = OTs) closely parallels *endo*-2-norbornyl toluene-*p*-sulphonate [3] in its solvolytic behaviour, but this point remains to be established.

The rate constant for buffered acetolysis of (12; R = OTs), $k_1(80°) = 9{\cdot}8 \times 10^{-5}$ sec.$^{-1}$, is of the same order of magnitude as for cyclohexyl toluene-*p*-sulphonate, and is 13 times that for (13; R = OTs), $k_1(80°) = 7{\cdot}4 \times 10^{-6}$ sec.$^{-1}$. However, a true measure of exactly how much more reactive (12; R = OTs) is compared with (13; R = OTs) must await a determination of the amount of ion-pair return involved.[3,14]

The solvolysis of (12 and 13; R = OTs) would therefore seem to represent an entry by way of a hydride shift mechanism into the 2-bicyclo[3,2,1]-/2-bicyclo[2,2,2]-octyl cationic system which has already been approached from two σ- [14,15] one π-,[16] and a ring-expansion route.[20] About this time in our work, Wiberg [21] reported that solvolysis of *exo*- and *endo*-6-bicyclo[3,1,1]heptylmethyl-*p*-bromobenzene sulphonate also

* In the ensuing discussion non-classical species are used for convenience and do not rule out in each case the possibility of equilibrating classical ions.

[14] H. L. Goering and M. F. Sloan, *J. Amer. Chem. Soc.*, 1961, **83**, 1397, 1992.
[15] H. M. Walborsky, J. Webb, and C. G. Pitt, *J. Org. Chem.*, 1963, **28**, 3214; H. M. Walborsky, M. E. Baum, and A. A. Youssef, *J. Amer. Chem. Soc.*, 1961, **83**, 988.
[16] S. Winstein and P. Carter, *J. Amer. Chem. Soc.*, 1961, **83**, 4485.
[17] G. Dann Sargent, *Quart. Rev.*, 1966, **20**, 301 and references cited therein.
[18] A. Streitweiser, 'Molecular Orbital Theory for Organic Chemists,' Wiley, New York, 1962, p. 386.
[19] R. Hoffmann, *J. Chem. Phys.*, 1964, **40**, 2480.
[20] J. A. Berson and D. Willner, *J. Amer. Chem. Soc.*, 1964, **86**, 609.
[21] K. B. Wiberg and B. A. Hess, jun., *J. Amer. Chem. Soc.*, 1966, **88**, 4433.

served as a route to the same system presumably by ring-expansion and hydride shift.*

Since our interest in this particular area of carbonium ion chemistry was occasioned by an attempt to interconnect several tetracyclic olefinic diterpenes, we decided to attempt a similar interconversion of bicyclo[3,2,1]oct-6-ene (A) and -2-ene (B), bicyclo[2,2,2]oct-2-ene (C) (see Table 1), and tricyclo[3,2,1,$0^{2,7}$]octane (15). Table 3 shows the results obtained from treating each

TABLE 3

Products from treatment of compounds (A)—(C) (Table 1) and (15) with HOAc–TsOH

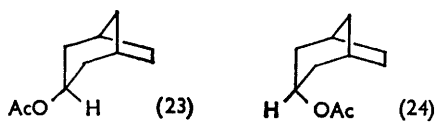
	(12; R = OAc)	(13; R = OAc)	(16; R = OAc)	(17; R = OAc)	(18; R = OAc)	(23 + 24)
(A)	37%	0	18%	18%	19%	8%
(B)	14%	0	25%	22%	27%	12%
(C)	13%	0	25%	22%	30%	10%
(15)	15%	0	23%	21%	30%	11%

TABLE 4

Chemical shifts of the CH_3CO_2 resonances in the bicyclo[3,2,1]- and bicyclo[2,2,2]-acetates

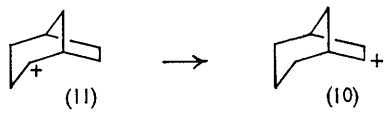
	(12; R = OAc)	(13; R = OAc)	(17; R = OAc)	(16; R = OAc)	(18; R = OAc)	(23)	(24)
CH_3COO chemical shift *	199·5	206·3	203·3	204·7	200·7	198·7	202·1

* c./sec. from internal tetramethylsilane at 100 Mc./sec.

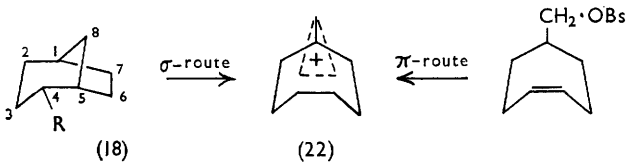


of these hydrocarbons for 24 hours with refluxing acetic acid containing toluene-*p*-sulphonic acid.

These reactions obviously differ markedly from the buffered acetolysis of (12 and 13; R = OTs) in the relatively high yield of *endo*-2-bicyclo[3,2,1]octyl acetate (18; R = OAc) and the corresponding *exo*-6-acetate (12; R = OAc).† Although the formation of (12; R = OAc) particularly from (B) and (C) is probably most easily explained by the initial formation of (15) followed by opening of the cyclopropane ring, it does raise the question of whether some of the *exo*-6-acetate (12; R = OAc) might not arise from a 6,4-hydride shift, *i.e.* (11) to (10), where (11) would be formed by protonation of, for example, (B).

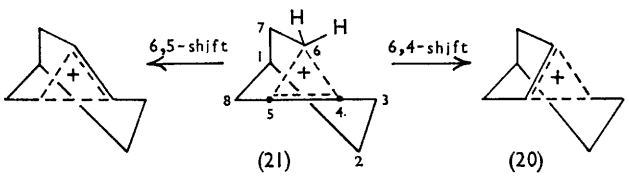


If one considers that partial bonding of the type associated with a non-classical species is a necessary criterion for this form of hydride shift, then a rearrangement of the type (11) ⟶ (10) would not be expected, for example, from a 2-bicyclo[3,2,1]-cation generated



from (18; R = OTs). The intermediate formed both from solvolysis of (18) (' σ-route ') and cyclohept-4-enylmethyl-*p*-bromobenzene sulphonate (' π-route ') [22] must have the structure represented by either (22) or the corresponding equilibrating classical cations; hence, it is not unexpected that a 6,4-hydride shift has not been detected, since C-6 is not one of the three centres involved (*viz.* C-1, C-4, and C-5).

This is not the case in the *exo*-2-bicyclo[3,2,1]-/2-bicyclo[2,2,2]-octyl cation, where C-6 *is* one of the three atomic centres involved [see (21) for example].



In this instance the two C-6 hydrogen atoms are *not* equivalent in the sense that a 6,5-hydride shift would produce the antipode of (21) whereas the alternative 6,4-shift would re-form (20). Berson [23] has recently produced compelling evidence against a 6,5-hydride shift being involved in the racemisation associated with the solvolysis of optically active (17; R = OTs), but in terms of a possible 6,4-shift, one can draw attention to the observation recorded by Walbrosky [15] that solvolysis of (17; R = OBs) gave (17; R = OAc) 54·1%, (16; R = OAc) 43%, (18; R = OAc) 1·7%, and 1·2% *of an unidentified component.*

EXPERIMENTAL

The n.m.r. spectra were recorded at 100 Mc./sec. on a Varian HA-100 spectrometer with internal proton stabilisation (tetramethylsilane) using dilute solutions (approximately 3 mole %) in deuteriochloroform, at a probe temperature of 33°. The calibration of the spectrometer was checked using a Hewlett-Packard electronic counter (5212A).

* Professor Wiberg mentions in this paper that his results are very similar to those found by Professor H. L. Goering and Dr. T. Padmanathan for the solvolysis of (12 and 13; R = OBs), unpublished results.

Note added in proof: Professor Goering has recently informed us that the results of his thorough and comprehensive examination of this problem will be published later this year.

† Goering and Sloan [14] have reported treating bicyclo[2,2,2]-oct-2-ene under these conditions, but make no mention of detecting (12; R = OAc).

[22] G. Le Ny, *Compt. rend.*, 1960, **251**, 1526.

[23] J. A. Berson and M. S. Poonian, *J. Amer. Chem. Soc.*, 1966, **88**, 170.

Chemical shift values for the methyl resonance (CH_3CO) of the acetate standards were derived from at least five recordings on an expanded scale (2 c./sec./cm.) and should be accurate to ±0·003 p.p.m. The composition of acetate mixtures was evaluated from peak areas and peak heights in the τ 8 region on the above scale expansion (mean of increasing and decreasing field sweep).

Melting points were determined in sealed capillary tubes. Infrared solution spectra were run in carbon tetrachloride by Mrs. F. Lawrie, Glasgow, on a Perkin-Elmer 225 spectrophotometer. Microanalyses were by Mr. J. M. L. Cameron, Glasgow, and his staff. Woelm Grade I alumina (neutral) was used for chromatography. For analytical and preparative thin-layer chromatography (t.l.c.) chromatoplates were spread with Kieselgel G (Merck). Gas–liquid chromatography (g.l.c.) was carried out using a Perkin-Elmer F 11 instrument fitted with a Carbowax 1540 support-coated open tubular column (50 ft.); carrier gas (N_2) flow rate was 4 ml./min., and oven temperatures were 50° (hydrocarbons) and 100° (alcohols and acetates). The reaction kinetics in buffered acetic acid were determined by the spectrometric method described by Swain and Morgan.[24]

exo-*Bicyclo*[3,2,1]*octan*-6-*ol* (12; R = OH).—A mixture of the epimeric bicyclo[3,2,1]octan-6-ols (25 : 1; g.l.c.) was prepared by the method of Wiberg and Hess.[13] Crystallisation from pentane afforded the predominating *exo*-isomer, m.p. 143—144·5° (lit.,[13] 144—145°); broadened doublet at τ 5·70 (H-6; *J* 7 c./sec.).

The exo-6-*acetate* (12; R = OAc) was prepared by reaction of the alcohol (98 mg.) with acetic anhydride (3 ml.) in dry pyridine (3 ml.), and the crude product (120 mg.) purified by short-path distillation; $[n]_D^{22}$ 1·4682, ill-resolved quartet at τ 5·07 (H-6; *J* 7 and 3 c./sec.) (Found: C, 71·1; H, 9·8. $C_{10}H_{16}O_2$ requires C, 71·4; H, 9·6%).

exo-6-*Bicyclo*[3,2,1]*octyl Toluene*-p-*sulphonate* (12; R = OTs).—Chilled solutions of *exo*-bicyclo[3,2,1]octan-6-ol (608 mg.) in dry pyridine (6 ml.) and toluene-*p*-sulphonyl chloride (1·225 g.) in the same solvent (5 ml.) were mixed and allowed to stand at room temperature overnight. The mixture was poured on ice, extracted with ether, and the solvent removed (traces of pyridine were expelled by azeotroping with benzene). The residual yellow oil crystallised slowly from methanol yielding the exo-*tosylate* (1·17 g.), m.p. 51—52°; quarter at τ 5·22 (H-6; *J* 7 and 3 c./sec.) (Found: C, 64·1; H, 7·0. $C_{15}H_{20}O_3S$ requires C, 64·3; H, 7·2%).

Bicyclo[3,2,1]*octan*-6-*one*.— *exo*-Bicyclo[3,2,1]octan-6-ol (1·20 g.) in acetone (20 ml.) was treated with Jones reagent [25] at 0° for 15 min. Normal work-up furnished bicyclo[3,2,1]-octan-6-one (1·02 g.) which was purified by vacuum-sublimation (70°/13 mm.), m.p. 153·5—157° (lit.,[13] 155—157°), $\nu_{max.}$ 1743 cm.$^{-1}$.

endo-*Bicyclo*[3,2,1]*octan*-6-*ol* (13; R = OH).—Bicyclo-[3,2,1]octan-6-one (674 mg.) was heated with an excess of lithium aluminium hydride in refluxing ether. The product, after vacuum-sublimation (655 mg.), was found (g.l.c.) to be a mixture of the *endo*- and *exo*-alcohols (93 : 7). Crystallisation from pentane yielded pure endo-*bicyclo*[3,2,1]-*octan*-6-*ol* (13; R = OH), m.p. 192—194°, $\nu_{max.}$ 3622 cm.$^{-1}$; multiplet at τ 5·50 (H-6; $W_{\frac{1}{2}}$ 22 c./sec.) (Found: C, 76·0; H, 11·1. $C_8H_{14}O$ requires C, 76·2; H, 11·2%).

The corresponding endo-6-*acetate* (13; R = OAc) was obtained in high yield by acetylation of the alcohol in pyridine and purified by short-path distillation *in vacuo*; $[n]_D^{23}$ 1·4672, multiplet at τ 4·90 (H-6; $W_{\frac{1}{2}}$ 22 c./sec.) (Found: C, 71·0; H, 9·4. $C_{10}H_{16}O_2$ requires C, 71·4; H, 9·6%).

endo-6-*Bicyclo*[3,2,1]*octyl Toluene*-p-*sulphonate* (13; R = OTs).—*endo*-Bicyclo[3,2,1]octan-6-ol (157 mg.) and toluene-*p*-sulphonyl chloride were treated in the manner described for the *exo*-isomer. The crude product crystallised from pentane giving the endo-*toluene*-p-*sulphonate* (13; R = OTs) (268 mg.), m.p. 43·5—44·5°; multiplet at τ 5·08 (H-6; $W_{\frac{1}{2}}$ 23 c./sec.) (Found: C, 64·3; H, 7·3%).

Bicyclo[3,2,1]*oct*-6-*ene*.—*exo*-6-Bicyclo[3,2,1]octyl toluene-*p*-sulphonate (12; R = OTs) (500 mg.) was heated in refluxing dry collidine (12 ml.) for 30 min. On cooling, water was added, and the reaction mixture extracted several times with pentane. The combined extracts were washed successively with dilute HCl, saturated $NaHCO_3$ solution, and then with water. The crude product obtained by drying of the solution and evaporation of the solvent *in vacuo* at 0° was allowed to sublime at −5° (760 mm.), giving *bicyclo*[3,2,1]*oct*-6-*ene* (125 mg.), m.p. 111—112° (lit.,[26] 106—108°); n.m.r. signals at τ 4·15 (sharp singlet; H-6, H-7) and 7·43 (broad singlet; H-1, H-5) (Found: *m/e* 108·09389. C_8H_{12} requires *m/e* 108·09390).

2-(1-*Pyrrolidinyl*)*bicyclo*[3,2,1]*octane*.—A solution of acraldehyde (10 g.) in dioxan (40 ml.) was added during 1 hr. to a stirred solution of 1-(1-pyrrolidinyl)cyclopentene [27] (20 g.) in dry dioxan (40 ml.) at 0°. After a further 3 hr., during which the mixture had attained room temperature, the solvent was removed *in vacuo* and the residual oil fractionated, to give 2-(1-pyrrolidinyl)bicyclo[3,2,1]octan-8-one (12·7 g.), b.p. 120—121°/0·1 mm. This keto-amine (12·0 g.) and hydrazine hydrate (18 ml.) were added to a solution of sodium (5·0 g.) in diethylene glycol (140 ml.). After heating at 140° for 1 hr., water and excess hydrazine hydrate were removed by distillation and the temperature was then maintained at 210° for a further 5 hr. The cooled mixture was diluted with water (450 ml.) and extracted with ether. After removal of the solvent, fractionation of the crude product furnished 2-(1-pyrrolidinyl)bicylo[3,2,1]-octane (7·23 g.), b.p. 86—88°/0·1 mm.

Bicyclo[3,2,1]*oct*-2-*ene*.— 2-(1-pyrrolidinyl)bicyclo[3,2,1]-octane (4·0 g.) and hydrogen peroxide (100 vol; 12 ml.) were heated in refluxing methanol (50 ml.) for 4 hr. The excess of peroxide was destroyed by the addition of a few mg. of 10% palladium–charcoal catalyst. Removal of the catalyst and then evaporation of solvent *in vacuo* gave the corresponding amine oxide which on pyrolysis (160°/0·1 mm.) yielded oily bicyclo[3,2,1]oct-2-ene (0·52 g.). Filtration of this oil in pentane through neutral alumina (Woelm grade I) and then sublimation at −5° (760 mm.) gave colourless plates, m.p. 42—44° (sealed capillary) (lit.,[28] 43—45°).

Bicyclo[3,2,1]*octan*-2-*one*.—A solution of 2-(1-pyrrolidinyl)bicyclo[3,2,1]octane (1·50 g.) and mercuric acetate (10·5 g.) in 5% aqueous acetic acid was stirred at 100° for 2½ hr. The yellow crystalline precipitate was filtered off, washed with 5% aqueous acetic acid, then with acetone, and the combined filtrates were evaporated to dryness

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under reduced pressure. Water (50 ml.) was added and hydrogen sulphide passed through the turbid solution until precipitation was complete. The mixture was filtered, the filtrate saturated with potassium carbonate, and the product extracted into ether. Sublimation (80°/16 mm.) of the crude product obtained by removal of the solvent afforded bicyclo[3,2,1]octan-2-one (530 mg.), m.p. 124—127° (lit.,[29] 127—129°).

exo- *and* endo-*Bicyclo*[3,2,1]*octan*-2-*ols* (16 and 18; R = OH).—Reaction of bicyclo[3,2,1]octan-2-one (400 mg.) with an excess of lithium aluminium hydride in refluxing ether [29] afforded a mixture (381 mg.) which was shown by g.l.c. to comprise *exo*-bicyclo[3,2,1]octan-2-ol (16; R = OH) (30%) and the corresponding *endo*-isomer (18; R = OH) (70%).

A sample of this mixture (102 mg.) was acetylated in the manner described previously.[29] The product, after short-path distillation (91 mg.), was submitted to quantitative analysis by n.m.r. and shown to consist of the *exo*- and *endo*-2-acetates in a ratio 3 : 7 (integration of CH_3COO signals).

Bicyclo[2,2,2]*oct*-5-*en*-2-*ol*.—Diels–Alder reaction of vinyl acetate (32 g.) and cyclohexa-1,3-diene (15 g.) using the procedure described by Goering and Sloan [14] furnished 2-acetoxybicyclo[2,2,2]oct-5-ene. Reaction of the crude acetate with lithium aluminium hydride led to bicyclo[2,2,2]-oct-5-en-2-ol (7·4 g.), which after crystallisation from light petroleum had m.p. 166—168° (6·2 g.) (lit.,[14] 167·5—169°).

Bicyclo[2,2,2]*octan*-2-*ol* (17; R = OH).—Bicyclo[2,2,2]-oct-5-en-2-ol (500 mg.) was hydrogenated over 10% Pd–C (50 mg.) in ethyl acetate (20 ml.); uptake was 1 mol. Recrystallisation of the product from pentane yielded bicyclo[2,2,2]octan-2-ol (436 mg.), m.p. 221·5—223° (lit.,[14] 221—222°).

The corresponding acetate [29] was prepared in the usual manner.

Bicyclo[2,2,2]*oct*-2-*ene*.—Bicyclo[2,2,2]oct-5-en-2-ol (840 mg.) was oxidised with Jones Reagent [25] at 0°. After work-up the crude product was converted into the *semicarbazone*, needles (from benzene) (440 mg.), m.p. 176—178° (Found: C, 60·2; H, 7·3; N, 23·5. $C_9H_{13}N_3O$ requires C, 60·3; H, 7·3; N, 23·5%).

The semicarbazone (406 mg.) in diethylene glycol (4 ml.) was heated at 100° until a homogeneous solution was obtained. Potassium hydroxide pellets (400 mg.) were added and the temperature was raised to 190° for 3½ hr. The crude olefin, which had completely sublimed into the reflux condenser, was recovered with pentane and then the solvent removed *in vacuo* at 0°. Sublimation of the residue (40°/760 mm.) furnished bicyclo[2,2,2]oct-2-ene (173 mg.), m.p. 114—116° (lit.,[30] 111—112°).

exo- *and* endo-*Bicyclo*[3,2,1]*octan*-3-*ols*.—Bicyclo[3,2,1]-octan-3-one [31] (216 mg.) and lithium aluminium hydride (100 mg.) reacted in refluxing ether. A mixture of the epimeric bicyclo[3,2,1]octan-3-ol (189 mg.) in a ratio 3 : 1 (g.l.c.) was obtained and separated by preparative t.l.c. (chloroform as solvent).

The predominating isomer, *exo*-bicyclo[3,2,1]octan-3-ol crystallised from pentane, m.p. 101—102° (lit.,[31] 101·5—102°). The *endo*-isomer, m.p. 203—204° (lit.,[31] 206—206·5°), also crystallised from pentane. Confirmation of structure assignments was obtained by n.m.r.[32]

The corresponding acetates were prepared by the standard procedure. exo-3-*Acetate* (Found: C, 71·2; H, 9·6. $C_{10}H_{16}O_2$ requires C, 71·4; H, 9·6%). endo-3-*Acetate* (Found: C, 71·1; H, 9·5%).

Tricyclo[3,2,1,$0^{2,7}$]*octane* (15).—Tricyclo[3,2,1,$0^{2,7}$]-octan-6-one [33] (1·5 g.) was heated with a solution of semicarbazide hydrochloride (2·25 g.) and hydrated sodium acetate (3·6 g.), in water (9 ml.) at 40° for 12 hr. The crude product was filtered off, and crystallised from aqueous ethanol to give the semicarbazone (1·52 g.).

Wolff-Kishner reduction of this derivative using the procedure described for the preparation of bicyclo[2,2,2]-oct-2-ene gave tricyclo[3,2,1,$0^{2,7}$]octane (422 mg.), which sublimed (−5°/760 mm.) as colourless needles, m.p. 87—89° (lit.,[34] 91—92°).

Buffered Acetolyses.—In a typical experiment, *exo*-6-bicyclo[3,2,1]octyltoluene-*p*-sulphonate (12; R = OTs) (93 mg.) was heated in acetic acid (5 ml.) containing sodium acetate (30 mg.) at 110° in a sealed ampoule for 18 hr. The reaction mixture was cooled, diluted with water, and extracted with pentane. The pentane extract was washed with aqueous sodium carbonate, dried, and the solvent removed. The products were separated by chromatography over silica gel into hydrocarbon (35—40% yield) and acetate (60—65% yield) fractions.

Unbuffered Acetolyses.—In a typical reaction, bicyclo-[2,2,2]oct-2-ene (20 mg.) was treated with acetic acid (2 ml.) containing toluene-*p*-sulphonic acid (2 mg.) at 110° in a sealed ampoule for 24 hr. The above work-up furnished high yields (80—90%) of acetate products. (Since aliquot sampling showed that the proportion of the products from bicyclo[3,2,1]oct-6-ene was still changing fairly rapidly even after a reaction time of 24 hr., the reaction was allowed to continue in this case for 1 week.)

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