STEREOCHEMICAL STUDIES. LX.*

STERIC COURSE OF BIMOLECULAR ELIMINATION IN BICYCLO[2.2.2]OCTYL 'ONIUM BASES AND TOSYLATES**

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The steric course of bimolecular elimination of the title compounds has been investigated using a variety of base–solvent combinations. Olefin is formed from the quaternary base in acceptable yields only with tert-butoxide in aprotic solvents and (as already reported) on pyrolysis of the quaternary hydroxide. Under these conditions, the elimination proceeds practically exclusively by a *syn*-mechanism; evidence is presented that this is largely or entirely a true E2 process and not a two-step reaction involving an ylide intermediate. An examination of the elimination behaviour of *trans*-3-methylbicyclo[2.2.2]octyl-2-trimethylammonium base and two open-chain 'onium compounds indicates that very specific structural features must be present for the two-step ylide mechanism to become favoured over an E2 process.

The contribution of bimolecular *syn*-elimination in the reaction of bicyclo[2.2.2]octyl tosylates is smaller than in the case of the corresponding 'onium base; its operation is favoured, relative to *anti*-elimination, in non-polar solvents.

Recently we reported the discovery of facile *syn*-elimination in reactions of cycloalkyl 'onium bases[3–7], bromides[8,9] and tosylates[10] leading to *trans*-cycloalkenes. Parallel with investigations on the steric course of elimination in open chain compounds[1,11–13], we initiated a study on some bicyclic systems, *i.e.* the 2-bicyclo[2.2.2]octyl 'onium bases *I* and *II* and the tosylate *III*, employing the appropriately β-deuterium labelled derivatives.

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** Published, in part, in preliminary form[1]. This is the nineteenth of a series of papers dealing with the mechanism of elimination reactions; for previous paper see ref.[2].

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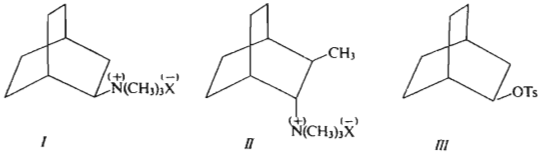


I *II* *III*

The geometry of the bicyclo[2.2.2]octyl skeleton is known[14] and allows a comparison between eliminations involving a ~ 0° and a ~120° torsion angle between the bonds undergoing fission. It is well established from work on this and related systems[15–23] that this structural feature favours *syn*-elimination relative to *anti*. We had found in our studies on the medium rings[3–10], as well as, subsequently, on open chain systems[11–13], that *syn*-elimination is a major contributor in the reactions leading to the *trans*-olefins, whereas the corresponding *cis*-olefins are formed, largely or predominantly, by *anti*-elimination. The question arose which, if any, features distinguish *syn*-elimination in the monocyclic or open chain systems leading to the *trans*-olefins from *syn*-elimination in the rigid, bicyclic, systems leading, necessarily, to a *cis*-olefin; the *syn*-elimination in the former systems being the result of "free choice" between two available alternatives, but in the latter being "torsionally enforced". For this and other reasons it was of interest to investigate the way in which the choice of the steric path of elimination in the bicyclic systems will depend on the nature of the leaving group, the base and the solvent employed.

EXPERIMENTAL

Bicyclo[2.2.2]octan-2-ol

A. *By hydroboration of bicyclo*[2.2.2]*oct-2-ene*[24]: A solution of the olefin (4·5 g, 0·042 mol) and sodium borohydride (1·2 g, 0·029 mol) in diglyme (40 ml) was treated with boron trifluoride etherate (4 g, 0·028 mol) in a nitrogen atmosphere under ice-cooling and stirring. The reaction mixture was stirred another 5 h at 0°C, treated, successively, with water (4 ml), 3M-NaOH (10 ml), 30% hydrogen peroxide and stirred for another hour at room temperature. The mixture was then diluted with five times its volume of water, the product taken up in ether, the ethereal extracts washed with water, dried and the solvent distilled off. The residue was purified by sublimation at 40°C/30 Torr and yielded 4·6 g (87%) of the product, m.p. 210—212°C (sealed capillary), lit.[24] 210—212°C.

B. *By reduction of* 2,3-*epoxybicyclo*[2.2.2]*octene*[24] with $LiAlH_4$–$AlCl_3$[25]: An ice-cooled and stirred solution of lithium aluminium hydride (3·1 g, 0·074 mol) in ether (80 ml) was treated with aluminium chloride (1·7 g, 0·013 mol) in ether (20 ml), followed by the above epoxide (5 g, 0·04 mol) in ether (10 ml). The mixture was stirred for 4 h at 0°C, followed by 4 hrs at room temperature. The usual work-up, followed by sublimation, afforded 4·3 g (84%) of the title compound, m.p. 210—212°C (sealed capillary).

Deuteriated Derivatives of Bicyclo[2.2.2]octan-2-ol

Bicyclo[2.2.2]octan-2-ol-*cis*-[3-D] was prepared by method *A* (above) using $NaBD_4$ and BF_3, bicyclo[2.2.2]octan-2-ol-*trans*-[3-D] by method *B* using $LiAlD_4$ and $AlCl_3$. Bicyclo[2.2.2]octyl 2-*p*-toluenesulphonate *cis*-[3-D] and *trans*-[3-D] were prepared from the corresponding alcohols as reported in the literature[26] for the un-labelled compound, m.p. 54–55°C, in agreement with the literature[26].

2-Dimethylaminobicyclo[2.2.2]octane

A solution of 2-aminobicyclo[2.2.2]octane[27] (1·2 g, 0·01 mol) in formic acid (60 ml) and 40% aqueous formaldehyde (50 ml) was refluxed for 24 h. The reaction mixture was acidified with conc. hydrochloric acid and taken to dryness. The residue was taken up in water (50 ml), the solution washed with ether, the aqueous layer made alkaline with conc. sodium hydroxide and the amine taken up in ether. The usual work-up afforded 0·7 g (61%) of the product, b.p. 82°C/14 Torr. For $C_{10}H_{19}N$ (153·3) calculated: 78·36% C, 12·50% H, 9·14% N; found: 78·35% C, 12·63% H, 8·84% N.

Methoiodide: Obtained in quantitative yield by allowing a solution of the tertiary amine (0·55 g) and methyl iodide (1·5 g) to stand at room temperature in the dark for 2 days and then diluting with light petroleum; m.p. 299–300°C (ethanol–ethyl acetate), lit.[27] 296°C.

2-Dimethylaminobicyclo[2.2.2]octane-*cis*-[3-D]

Bicyclo[2.2.2]octene[24] was treated with diborane-[D_6] and the alkylborane solution obtained decomposed using chloramine[28] as recently reported by Coke and Cooke[23]. The crude amine, obtained in 22% yield was methylated as described above for the deuterium-free compound.

trans-3-Amino-2-methylbicyclo[2.2.2]octane

To a stirred two-layer solution of *trans*-2-methylbicyclo-[2.2.2]octane-3-carboxylic acid[29] (4·25 g) in chloroform (40 ml) and conc. sulphuric acid (40 ml) sodium azide (8·9 g) was added under the same conditions as described previously[29] for the isomeric mixture of the acids. The usual work-up afforded 2·8 g (80%) of the amine, b.p. 86°C/13 Torr, which solidified on standing. The product was analysed in the form of its *hydrochloride*, m.p. 305–307°C (sealed capillary). For $C_9H_{18}ClN$ (175·7) calculated: 61·52% C, 10·32% H, 7·97% N; found: 61·54% C, 10·43% H, 7·97% N.

trans-3-Dimethylamino-2-methylbicyclo[2.2.2]octane

The Clarke-Eschweiler methylation of the above amine gave the dimethylamine, b.p. 86–87°C/10 Torr in 51% yield. For $C_{11}H_{21}N$ (167·3) calculated: 78·97% C, 12·65% H, 8·37% N; found: 78·72% C, 12·71% H, 8·55% N.

Methoiodide: The amine was refluxed with methyl iodide in methanol. The reaction mixture was taken down and purified by dissolving in a little methanol and precipitating with ether, m.p. 274·5–275·5°C. For $C_{12}H_{24}IN$ (309·2) calculated: 46·67% C, 7·82% H, 4·60% N; found: 46·63% C, 7·67% H, 4·44% N.

trans-3-Dimethylamino-2-methylbicyclo[2.2.2]octane-[2-D]

2-Methylbicyclo[2.2.2]oct-2-ene[29] (7·72 g, 0·063 mol) in diglyme (120 ml) was treated with diborane-[D_6], generated *in situ* from sodium borodeuteride (2·19 g, 0·052 mol) and boron

trifluoride etherate (9·87 g, 0·064 mol). The resulting alkylborane solution was decomposed by chloramine solution[28] (0·063 mol) and the amine isolated in the usual manner[7]. The crude amine obtained in 5·9% yield was methylated as described above for the deuterium free compound.

Methyl Di-n-butylacetate-[2-D]

A solution of di-n-butylmalonic acid[30] (70 g, 0·33 mol) in ether (500 ml) was shaken for 5 minutes with 20 ml (1 mol) of deuterium oxide and this operation was repeated ten times. The ether was distilled off under exclusion of moisture and the residue decarboxylated as reported[30] for the unlabelled substance. The crude product was esterified using ethereal diazomethane and the product distilled, b.p. 92°C/10 Torr, yield 40 g (65%), homogeneous by v.p.c. For $C_{11}H_{21}DO_2$ (186·3) calculated: 70·92% C, 11·90% H(D); found: 70·59% C, 12·03% H(D).

2-n-Butylhexan-1-ol-[2-D]

Reduction of the above ester with lithium aluminium hydride in ether in the usual manner, followed by distillation (b.p. 112°C/15 Torr) afforded the pure (v.p.c.) alcohol in 94% yield. According to mass spectrometric analysis it contains 94·2% of the d_1 species, the remainder being unlabelled. For $C_{10}H_{21}DO$ (142·3) calculated: 75·88% C, 14·01% H(D); found: 75·92% C, 13·75% H(D).

2-n-Butyldimethylaminohexane-[2-D]

The above alcohol was converted into the *p*-toluene-sulphonyl ester in the usual manner in pyridine. It was obtained in 77% yield and was an oil. A solution of the tosylate (38·3 g, 0·11 mol) in dimethyl sulphoxide (80 ml) was added to a solution of sodium azide (27 g, 0·41 mol) and sodium hydrogen carbonate (7 g) in dimethyl sulphoxide (450 ml) and kept at 90°C. After 4 hours at this temperature, the mixture was diluted with about 5 litres of saturated sodium chloride solution and the product taken up in ether. The ethereal solution was washed with water, dried, the ether distilled off and the crude azide reduced to the amine using ethereal lithium aluminium hydride under the standard conditions. The standard Clarke-Eschweiler methylation procedure (*cf.* above) afforded 14·2 g (70%) of the dimethylamino derivative, b.p. 95°C/12 Torr. The product is homogeneous by v.p.c. and was shown by mass spectrometry to contain 94·9% of a d_1 species. For $C_{12}H_{26}DN$ (185·4) calculated: 77·76% C, 14·68% H(D), 7·56% N; found: 77·42% C, 14·71% H(D), 7·35% N.

The *methoiodide* was obtained by reaction with methyl iodide for 48 h in benzene; m.p. 173 to 175°C. For $C_{13}H_{29}DIN$ (377·3) calculated: 47·70% C, 9·24% H(D), 4·28% N; found: 47·48% C, 9·37% H(D), 4·30% N.

2,2-Di-tert-butylethanol-[2-D]

This compound was prepared from 1,1-di-tert-butylethylene by deuterioboration, exactly as described[31] for the deuterium free compound, in 62% yield. The product contains 6·6% d_0, 91·1% d_1 and 2·3% d_2 species; m.p. 52—54°C, in agreement with the literature[31].

2,2-*Di-tert-butylethyl*-2-D *p-toluenesulphonate* was prepared by the standard procedure in 86% yield., m.p. 78—79°C.

2,2-Di-tert-butyldimethylaminoethane-[2-D]

The above tosylate was converted to the azide, this was reduced to the amine and the amine methylated by the procedures reported above for the case of the analogous straight chain compounds;

15·6 g of the tosylate gave 6·2 g of the title compound, b.p. 80°C/10 Torr; it contains 4·8% d_0, 92·0 d_1 and 3·2% d_2 species. For $C_{12}H_{26}DN$ (185·4) calculated: 77·76% C, 14·68% H(D), 7·56% N; found: 77·71% C, 14·95% H(D), 7·60% N.

Methoiodide: A solution of the tertiary amine (2·75 g) and methyl iodide (10 ml) in benzene was kept at 50°C for 8 days. The separated crystals were filtered off and washed with pentane; yield 4·1 g (84%), m.p. 237–239°C (sealed capillary), reported[32] m.p. 239°C.

Quaternary Chlorides

The title compounds prepared from the corresponding quaternary iodides in the usual manner[4] are very hygroscopic and could not be analysed. They were dried carefully over phosphorus pentoxide on the oil pump previous to the elimination reaction.

Elimination Runs

All elimination reactions were carried out under nitrogen in sealed tubes. The conditions employed (concentration, time and temperature) were analogous as described by us previously[7,10], except for 2-bicyclo[2.2.2]octyl tosylates. The resulting olefins and trimethylamine were isolated by standard procedures[7,10]. The olefins thus obtained were further purified by sublimation or distillation.

RESULTS AND DISCUSSION

Onium Bases

The steric course of the elimination of *exo*-norbornyltrimethylammonium hydroxide has been investigated some time ago[22]; after the experimental work described in this paper had been concluded a study of the steric course of the elimination of the 2-bicyclo[2.2.2]octyltrimethylammonium hydroxide was also reported[23]. This relates to reactions under pyrolytic conditions; in these processes norbornene as well as bicyclo[2.2.2]octene formation takes place exclusively by *syn*-elimination.

We have examined the behaviour of the quaternary base *I* under homogeneous conditions, in the base–solvent systems listed in Table I. With methoxide–methanol and tert-butoxide–tert-butanol the yield of bicyclo[2.2.2]octene was only about 1 and 7%, respectively (Table I). The yields were considerably higher when aprotic solvents were employed: with tert-butoxide in dimethyl sulphoxide and in benzene the yields were 50 and 70%, respectively; under pyrolytic conditions the yield of the olefin (as isolated) was 36%. The elimination under the latter three conditions was then carried out using the *cis*-β-deuterium labelled substrate. The olefin formed was in each case practically deuterium free: the elimination thus proceeded exclusively by a *syn*-elimination mechanism in spite of the fact that this elimination mode is slowed down by the isotope effect.*

* For the *syn*-elimination reaction of the corresponding norbornyl system the value of this isotope effect has been found[23] to be 1·9.

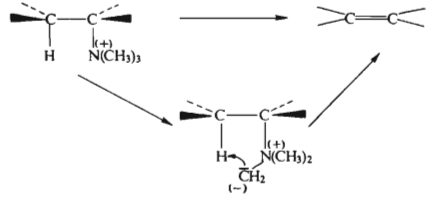
TABLE I

Bimolecular Elimination of 2-Bicyclo[2.2.2]octyltrimethylammonium Chlorides (*I*) and *trans*-3-Methylbicyclo-[2.2.2]octyl-2-trimethylammonium Chlorides (*II*)

Substrate	Conditions	% E2[a]	% d_0 in olefin[b]	*d*-Composition in trimethylamine[c]			
				% d_0	% d_1	% d_2	% d_3
I	CH_3OK/CH_3OH	1[e]	—	—	—	—	—
I	t-C_4H_9OK/t-C_4H_9OH	7·5[e]	—	—	—	—	—
I[d]	t-$C_4H_9OK/(CH_3)_2SO$	50[e]	100	99·9	0·1	—	—
I[d]	t-C_4H_9OK/C_6H_6	70[e]	100	61·9	28·1	8·4	1·7
I[d]	pyrolysis	36[f]	99·2	70·5	24·5	5·0	—
II	t-C_4H_9OK/t-C_4H_9OH	1·9[e]	—	—	—	—	—
II[g]	t-$C_4H_9OK/(CH_3)_2SO$	40[e]	100	97·4	2·6	—	—

[a] The yield of olefin from the non-deuterated substrate, the other product being the dimethylamino derivative formed by substitution on methyl. [b] Deuterium content determined by mass spectrometry, in the olefin formed from *cis*-β-deuterated derivative of *I* and *II*. [c] Trimethylamine formed in the reaction of the *cis*-β-deuterated derivative of *I* and *II*. [d] The starting 2-dimethylaminobicyclo[2.2.2]octane contains 91·4% d_1. [e] As determined by v.p.c. [f] As isolated. [g] The starting 3-dimethylamino-2-methylbicyclo[2.2.2]octane contains 94·6% d_1.

Both a genuine one-step as well as a two-step (ylide) mechanism[33-35] (Scheme 1) must be considered for the *syn*-elimination. The operation of the ylide mechanism would be revealed by the presence of deuterium in the trimethylamine set free in the elimination[34,35]. The trimethylamine obtained from the reaction in dimethyl sulphoxide was found to be deuterium free, proving complete absence of an ylide mechanism; by contrast, the trimethylamine isolated from the reaction in benzene, as well as from the pyrolysis run, was found to contain considerable amounts of a d_1 species (28·1 and 24·5%, respectively); however, in both these cases there were,

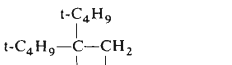


SCHEME 1

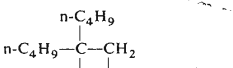
in addition, also trimethylamine-d_2 and -d_3 present, indicating that incorporation of deuterium has taken place, largely or exclusively, by exchange on the quaternary 'onium base, *i.e.* previous to elimination. We thus conclude that the *syn*-elimination proceeds, at least to a large extent, by a one-step mechanism. Coke and Cooke[23] have analogously concluded that the *syn*-elimination leading to bicyclo[2.2.2]-octene by the pyrolysis of *I* proceeds to no more than 13% by an ylide mechanism.

The elimination behaviour of the compound *II* was next investigated. In this system, *syn*-elimination is the only path possible; however, E2 *syn*-elimination is believed to proceed by way of a transition state in which the carbon C_β has some carbanion character[36,37] and the presence of the methyl group should hence make this mechanism less favourable[38]. Therefore, the question of interest in the behaviour of the compound *II* appeared whether the two-step ylide mechanism has not taken over. The elimination in dimethyl sulphoxide–tert-butoxide base–solvent system employing the β-deuterium labelled derivative showed that this was not the case: less than 3% of the elimination has taken place by an ylide mechanism.

In this context, the problem of the requirements (steric and/or electronic) for the ylide mechanism may be reconsidered. It follows from the above results that the presence both of enforced coplanarity and of a β-hydrogen located on a tertiary carbon does not necessarily suffice to make the ylide mechanism favoured over the E2 *syn*-mechanism. To our knowledge a single compound has been found so far which – under pyrolytic conditions* – reacts predominantly by the two-step ylide mechanism, *i.e.* the quaternary base of the β,β-di-tert-butylethyl system[34] *IV*.



IV



V

We have now examined the elimination of the deuterated compound *IV* in homogeneous aprotic solution (potassium tert-butoxide in dimethyl sulphoxide) and found a practically exclusive operation of ylide type elimination.** In striking contrast, in the reaction of the corresponding labelled β,β-di-n-butylethyl 'onium base *V* the contribution of the ylide mechanism was negligible. Under pyrolytic conditions,

* When the reactions are carried out in ether using a lithium alkyl as base the ylide mechanism becomes more frequent[35].

** Under pyrolytic condition, American authors found about 70% contribution of the ylide path.

the contrast between the compounds *IV* and *V* was less striking* but even so the results show clearly that here, too, the tendency for the two-step mechanism is much greater in the reaction of the highly branched system *IV*. (Table II).

TABLE II

Bimolecular Elimination of 2,2-Di-tert-butylethyl-1-trimethylammonium Chloride-[2-D] (*IV*) and 2,2-Di-n-butylethyl-1-trimethylammonium Chloride-[2-D] (*V*)

Compound	Reaction conditions	% Olefin[a]	*d*-Composition in trimethylamine[b]		
			d_0	d_1	d_2
IV	pyrolysis	50	34·7	61·5	3·8
V		23	76·0	23·0	1·0
IV	$t\text{-}C_4H_9OK/(CH_3)_2SO$	58	1·6	98·4	0·0
V		15	99·2	0·8	0·0
IV	$t\text{-}C_4H_9OK/t\text{-}C_4H_9OH$	0·5	—	—	—
V		0·5	—	—	—
IV	CH_3OK/CH_3OH	0·4	—	—	—
V		0·9	—	—	—

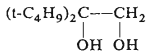
[a] Determined by v.p.c., [b] corrected for incomplete labelling of the starting compound.

Under the aprotic conditions now investigated, the yields of olefins range between 15–58%, being significantly higher for system *IV*. On the other hand, in the elimination reactions using protic base–solvent combination (tert-butoxide in tert-butanol and methoxide in methanol, respectively) only negligibly small amounts of olefin were found, the yields being approximately the same for the substrates *IV* and *V*.

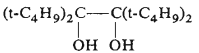
It would seem therefore that at least four conditions have to be fulfilled for the ylide mechanism to contribute to an important degree. One is enforced *syn*-planarity of the bonds to be broken (this feature not only enhances *syn*-elimination but also slows down *anti*-elimination). A second condition is that approach of an external base to the β-hydrogen is made difficult[23] (as by the di-tert-butyl substitution in

* No attempts have been made by us to preclude deuterium scrambling in the course of the elimination reaction due to the isotopic exchange on the starting 'onium base. Therefore, the actual contribution of the ylide mechanism might be considerably lower.

compound *IV*), allowing the internal base to compete.* A third condition appears to be that the β-hydrogen and the 'onium group approach each other closely. Simple geometric consideration shows that this will be the case in the di-tert-butyl derivative *IV*. Some support for this view may be found in the fact that in the structurally related diols *VI* and *VII* intramolecular hydrogen bonds of exceptional strength have been detected by infrared spectroscopy[40].



VI



VII

Finally, aprotic conditions seem to be necessary for the ylide elimination to compete succesfully with other mechanistic alternatives, even if the above three conditions are fulfilled.**

Tosylates

Studies of the steric course of elimination of *exo*-2-bicyclo[2.2.1]heptyl tosylate have been reported previously[19,41]. The reaction has been found to proceed, in part or largely, by *syn*-elimination, depending on the reaction conditions employed.*** We now report results of a study on the bicyclo[2.2.2]octyl tosylates, using both *cis*- and *trans*-3-D labelled derivatives. The reaction was carried out in four different base–solvent combinations and the data are listed in Table III.

As may be seen simply by considering the deuterium content of the olefin isolated from the reaction of the labelled compounds, *syn*-elimination does operate, in varying degree, under all conditions investigated. Using the data obtained for both *cis*- and *trans*-deuterated compounds, the approximate contribution of *syn*-elimination in the parent non-deuterated substrate can be calculated, assuming that $(k_H/k_D)_{syn} = (k_H/k_D)_{anti}$.† Thus calculated values are listed in column 5 of Table III.

It is immediately evident from these data that *syn*-mechanism contributes consider-

* A support for the view that these two conditions alone are not sufficient is provided by the fact that 2-*endo*-norbornyltrimethylammonium hydroxide on pyrolysis gives only a negligibly low yield of an elimination product[39].

** On the other hand, if especially favourable conditions for the preferential formation of the ylide intermediate are afforded and, at the same time, the backward protonisation reaction of the ylide is completely precluded, using extremely strong bases, *e.g.* alkyllithium reagents, the ylide type mechanism may appear to be dominating even in the structurally simple 'onium salts[35].

*** In contrast, elimination of the corresponding *endo*-derivative has been found to proceed, largely or exclusively, in *anti*-fashion[41].

† There is considerable evidence from other systems that the deuterium isotope effect for *syn*-elimination is lower than for *anti*-elimination[13,37,42]. The calculated figures for % *syn* in the d_0-substrate given in Table III therefore represent maximum values.

TABLE III

Bimolecular Elimination of 2-Bicyclo[2.2.2]octyl *p*-Toluenesulphonate-*cis*-[3-D] and -*trans*-[3-D] using Potassium tert-Butoxide in Different Solvents

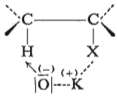
Compound	Solvent	Conditions[a]	% d_1 in olefin	% *syn*-H[b]
cis-3-D[c]	$HCON(CH_3)_2$	(8 h) 75°C	63·8	
trans-3-D[d]			82·7	61
cis-3-D[c]	$(CH_3)_2SO$	(8 h) 75°C	77·4	
trans-3-D[d]			92·4	64
cis-3-D[c]	$(CH_3OCH_2CH_2)_2O$	(22 h) 130°C	28·8	
trans-3-D[d]			92·6	85
cis-3-D[c]	C_6H_6	(120 h) 150°C	15·9	
trans-3-D[d]			90·9	89

[a] The tosylate (300 mg) was heated with 10 ml of a 0·5M solution of potassium tert-butoxide in the solvent indicated. [b] Percentage of *syn*-elimination in the unlabelled substrate (H) calculated from the data in column 4 (corrected for incomplete deuteration of the reactant, *cf.* notes *c* and *d*) using the expression

$$\frac{\%\ syn}{\%\ anti} = \left(\frac{d_0}{d_1}\right)^{1/2}_{cis} \Big/ \left(\frac{d_0}{d_1}\right)^{1/2}_{trans}.$$

[c] The starting labelled bicyclo[2.2.2]octanol contains 92% d_1. [d] The starting labelled bicyclo[2.2.2] octanol contains 97·6% d_1.

ably to the overall elimination process even in the parent 2-bicyclo[2.2.2]octyl tosylate, resembling thus the reported[19,41] behaviour of the corresponding *exo*-bicyclo[2.2.1]heptyl system. Moreover, as may be seen from the present data, there is a pronounced increase in the contribution of the *syn*-mechanism on going from strongly dissociating dipolar solvents dimethylformamide and dimethyl sulphoxide to less dissociating diglyme and non-dissociating benzene. The analogous trend has been observed by us before in the reaction of some alicyclic[8–10] as well as open-chain[1,13] tosylates and bromides and been interpreted as showing that *syn*-elimination is favoured by ion-pairing of the attacking base, since this facilitates a "pseudo-cyclic" mechanism as shown (Scheme 2).



SCHEME 2

It is of interest to compare the factors controlling the steric course of elimination in the bicyclo[2.2.2]octyl and *exo*-bicyclo[2.2.1]heptyl systems.* It is clear from the data reported and cited in the present paper that the elimination behaviour in these two systems is closely similar. In the bicyclo[2.2.2]octyl system *syn*-elimination is favoured by enforced co-planarity, in the bicyclo[2.2.1]heptyl system by this stereoelectronic factor and/or the greater accessibility of the *exo*-hydrogen. The claim has recently been made[41] that "the predominant *exo-syn* elimination for the *exo*-norbornyl tosylates is primarily a consequence of the greater accessibility of the *exo*-hydrogen and not due to any stereoelectronic factors favouring *syn*-elimination". The present comparison suggests that both factors presumably play a role. Moreover, the present data clearly indicate the important role of the common solvent effect submerged by other (steric and/or polar) specific structural features of individual substrates.

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* In case of the tosylates a direct comparison is not possible since somewhat different conditions were employed in the two cases.

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